THE

LONDON, EDINBURGH, AND DUBLIN

PHILOSOPHICAL MAGAZINE

AND

JOURNAL OF SCIENCE.

[SEVENTH SERIES.]

APRIL 1935.

LVII. *The Behaviour of Electrons in Chlorine.* *By* V. A. BAILEY, *M.A.*, *D.Phil.* (*Oxon*), *F.Inst.P.*, *Associate Professor of Physics, University of Sydney, and* R. H. HEALEY, *M.Sc.*, *Demonstrator in Physics, University of Sydney* *.

1. AMONG the gases to which the methods of investigation † developed in Sydney have not yet been applied one of the most interesting is chlorine, for it is an elementary gas which has great chemical activity, lacks optical absorption in the infra-red region, and is supposed by some physicists to have a large "electron-affinity." Accordingly special apparatus has been constructed for the purpose of applying these methods to chlorine.

A diffusion instrument with three successive slits was constructed of brass plated with platinum, and is similar to the instrument described previously ‡. The construction of the present instrument, however, is simpler, because the electrodes are fixed.

* Communicated by the Authors.

† V. A. Bailey and J. D. McGee, Phil. Mag. vi. p. 1073 (1928); V. A. Bailey and W. E. Duncanson, Phil. Mag. x. p. 145 (1930); V. A. Bailey and J. B. Rudd, Phil. Mag. xiv. p. 1033 (1932); and V. A. Bailey and J. M. Somerville, Phil. Mag. xvii. p. 1169 (1934).

‡ V. A. Bailey and J. D. McGee, *loc. cit.*

On account of the activity of the gas, the mercury gauges usual in this kind of work were replaced by brass spiral Bourdon gauges, and the movement of each was observed by means of a mirror, lamp, and scale. These gauges are sensitive to 0·05 mm. of mercury, and so, with the help of an auxiliary small known volume, it was possible to admit to the diffusion instrument a quantity of gas as low as 0·1 mm. known accurately to within 1 per cent.

Liquid air traps and vacuum taps were so arranged that the gas could be easily moved from one place to another, the pumping being done by means of a two-stage Pfeiffer rotary oil-pump. The pump was protected from the gas by means of two such traps, and, in addition, a trap containing solid caustic potash. After use, the chlorine was removed to an evacuated flask containing 25 c.c. of mercury.

The spiral gauges were standardized by means of hydrogen, using mercury gauges which were temporarily attached for the purpose, and were found to work admirably under all circumstances.

The auxiliary volumes and that of the instrument were compared accurately by means of all these gauges.

The whole apparatus, including the magnetizing coils, was then tested by means of hydrogen, whose properties in respect of the motion of electrons in it are well established.

The chlorine to be investigated was obtained from a quantity of pure gold chloride which had been kindly prepared for us by Mr. L. W. O. Martin, B.Sc. The chloride was heated *in vacuo* to a temperature of about 200° C. by means of a paraffin oil bath, and the issuing chlorine was condensed immediately in a side tube containing P_2O_5. The tap between this generator and the rest of the apparatus was lubricated with moist P_2O_5 and graphite. When sufficient gas had been condensed it was admitted to a glass reservoir, of about one litre capacity, containing some P_2O_5.

Some preliminary experiments were undertaken, primarily with the purpose of finding what kind of surface in the presence of chlorine would be most suitable for emitting electrons under the influence of ultra-violet light. Following Wulf *, a silver surface was tried, and

* Th. Wulf, *Annalen der Physik*, Bd. 9, Heft 12, p. 946 (1902).

finally adopted. The distribution ratios S_1 and S_2* were observed for different pressures and electric forces, with the results shown in Table I.

From the fact that in all these observations S_1 is notably less than S_2, it is clear that free electrons were present in notable proportions even after traversing several centimetres of the gas at pressures of 1 mm. or more.

TABLE I.

Z.	p.	Z/p.	S_1.	S_2.	R.	V_g.
10	1·0	10	0·14	0·20	0·72	5
5·0	1·0	5	0·50	0·60	0·61	285
5·0	3·3	1·5	0·34	0·52	0·61	356
5·5	0·5*	11*	0·33	0·58	0·63	440

* Approximate value.

Observations were also made of the magnetic intensity H_0 required to make $S_2=R$, where R is the normal distribution ratio, that is, the distribution ratio for a stream containing only ions. The results of these observations are given in Table II.

TABLE II.

Z.	p.	Z/p.	H_0.	λ.	V_g.
				per cent.	
5·0	0·1	50	200	12·8	12
5·0	1·0	5	600	1·3	342
5·0	3·3	1·5	750	0·8	370
5·5	0·5	11	385	3·8	440

From the numbers shown in the column under H_0 it may be seen that with magnetic forces of only a few hundred gauss a notable effect is produced on the lateral diffusion of the streams; this is additional proof of the conclusion that with values of the ratio Z/p from 1·5 to 11 many free electrons exist at pressures of chlorine of about 1 mm. or more. In the fifth column of Table II. are given approximate values of λ, the average proportion of its own energy lost by an electron in a collision with a chlorine molecule.

* See Table III. for the definitions of S_1 and S_2.

These measurements had to be made very rapidly, for it was found that the pressure of the gas in the instrument diminished at a considerable rate. Accordingly it was decided to make observations on mixtures of chlorine with other gases whose properties are known and with which chlorine has no chemical interaction. In this way it was found possible to diminish the rate of disappearance of chlorine sufficiently to allow accurate measurements to be made.

During the first observations on pure chlorine the photo-electric effect was adequate, but after two days it had diminished so much that in order to obtain conveniently measurable currents it was necessary to increase the potential difference V_g between the grid and silver surface from a few volts to about 400 volts, as shown in the last column of Tables I. and II.

A similar behaviour was also found to occur with the gas mixtures studied, so it was necessary to restore the photo-electric sensitivity at intervals of not less than two weeks by admitting about 3 mm. of hydrogen to the instrument and passing a discharge of about 10 milli-amperes for two minutes between the silver surface and the grid, with the former at a negative potential ; after restoration the hydrogen was pumped out again.

2. *Methods of Investigations.*

For facility of reference we give in the following table a list of the principal symbols used in the discussion and their definitions :—

TABLE III.

p=pressure of gas, in mm. of mercury.

Z=electric intensity, in volts/cm.

$\zeta = Z/p$.

S_1=fraction of the stream in the first diffusion chamber which passes out of the chamber ; also called the distribution ratio.

S_2=corresponding fraction for the second diffusion chamber.

R=the distribution ratio with negative ions for either chamber.

H_0=the magnetic intensity required to make S_2 (and S_1) equal to R.

k=mean energy of agitation of an electron in terms of the mean energy of agitation of a molecule at 15° C.

W=the drift velocity of an electron in the direction of Z, in cm./sec.

α=probability of attachment of an electron to a molecule per unit length of its motion in the direction of Z.

u=the mean velocity of agitation of an electron, in cm./sec.

L=the mean free path of an electron in the gas at 1 mm. pressure, in cm.

λ=the mean proportion of its own energy lost by an electron at a collision with a gas-molecule.

h=the probability of an electron becoming attached to the molecule with which it collides.

In the earlier part of our investigations on mixtures of chlorine with other gases two different methods were used, which have been described in previous publications *. In the following, for the sake of brevity, we shall refer to them by the adjectives " original " and " magnetic."

Since, at the lower pressures, the chlorine tended to disappear proportionately more rapidly during each pair of observations necessary to determine k, it was considered desirable also to use a method which would require only one observation at a given pressure. This method we now proceed to describe.

Two mixtures are prepared, one containing the proportion f_a of a gas A of known properties and the proportion g_a of the gas X whose properties have to be determined, and the other containing the proportion f_b of a gas B of known properties and the proportion g_b of the gas X. Thus

$$g_a=1-f_a, \quad g_b=1-f_b.$$

For some definite value of k let L_1 and λ_1 be the values respectively of the quantities L and λ (defined in Table III.) in the first mixture, and L_2 and λ_2 the values in the second mixture. For the same value of k let the values of L and λ for the gases A, B, and X be respectively (L_a, λ_a) (L_b, λ_b), (L_x, λ_x).

By considering the number of collisions L^{-1} made by an electron whose total path is one centimetre, and the amount of energy $L^{-1}\lambda k$ lost in these collisions, it is easy to derive the following pairs of equations :—

$$\left.\begin{aligned} L_1^{-1}&=f_aL_a^{-1}+g_aL_x^{-1}, \\ L_2^{-1}&=f_bL_b^{-1}+g_bL_x^{-1}\ ; \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (1)$$

$$\left.\begin{aligned} \lambda_1L_1^{-1}&=f_a\lambda_aL_a^{-1}+g_a\lambda_xL_x^{-1}, \\ \lambda_2L_2^{-1}&=f_b\lambda_bL_b^{-1}+g_b\lambda_xL_x. \end{aligned}\right\} \quad . \quad . \quad . \quad . \quad . \quad (2)$$

* V. A. Bailey, Phil. Mag. i. p. 825 (1925); V. A. Bailey and A. J. Higgs, Phil. Mag. vii. p. 281 (1929); J. D. McGee and J. C. Jaeger, Phil. Mag. vi. p. 1107 (1928); and V. A. Bailey and J. B. Rudd, *loc. cit.*

The following relations, which have been previously * given, are also true :—

$$L=8\times10^{-9}W\sqrt{k}\zeta^{-1}, \quad . \quad . \quad . \quad . \quad . \quad (3)$$

$$\lambda=1{\cdot}86\times10^{-14}W^2k^{-1}, \quad . \quad . \quad . \quad . \quad . \quad (4)$$

where $\zeta=Z/p$.

Therefore

$$L^{-1}=s, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

$$\lambda L^{-1}=t, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where

$$s=17k^{-1}\zeta\lambda^{-\frac{1}{2}} \text{ and } t=17k^{-1}\zeta\lambda^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad (7)$$

On using the relations (5) and (6) to eliminate the quantities L_1 and L_2 from equations (1) and (2), and the following notation :

$$\left.\begin{array}{ll} q_a=\rho_a L_a^{-1}, & q_b=\rho_b L_b^{-1}, \\ r_a=\rho_a\lambda_a L_a^{-1}, & r_b=\rho_b\lambda_b L_b^{-1}, \\ \text{where} \quad \rho_a=g_a^{-1}-1 \quad \text{and} & \rho_b=g_b^{-1}-1, \end{array}\right\} \quad . \quad . \quad (8)$$

the equations (1) and (2) become

$$s_1g_a^{-1}=q_a+L_x^{-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (9)$$

$$s_2g_b^{-1}=q_b+L_x^{-1}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (10)$$

$$t_1g_a^{-1}=r_a+\lambda_xL_x^{-1}, \quad . \quad . \quad . \quad . \quad . \quad (11)$$

$$t_2g_b^{-1}=r_b+\lambda_xL_x^{-1}. \quad . \quad . \quad . \quad . \quad . \quad (12)$$

From equations (9) and (11) we derive the following :—

$$L_x=\frac{1}{s_1g_a^{-1}-q_a}, \quad . \quad . \quad . \quad . \quad . \quad (13)$$

$$\lambda_x=\frac{t_1g_a^{-1}-r_a}{s_1g_a^{-1}-q_a}. \quad . \quad . \quad . \quad . \quad . \quad (14)$$

On eliminating L_x^{-1} between (9) and (10) and $\lambda_xL_x^{-1}$ between (11) and (12) we obtain the following equations :—

$$q_a-q_b=s_1g_a^{-1}-s_2g_b^{-1}, \quad . \quad . \quad . \quad . \quad (15)$$

$$r_a-r_b=t_1g_a^{-1}-t_2g_b^{-1}. \quad . \quad . \quad . \quad . \quad (16)$$

* V. A. Bailey and W. E. Duncanson, *loc. cit.* They are derived from the well-known formulæ : $W=\cdot815\ Zel/mu$, $\lambda=2{\cdot}46\ W^2/u^2$.

The quantities λ, Z, H_0, and k are also related, as follows * :—

$$\lambda^{\frac{1}{2}}=13{\cdot}6(Z/H_0)(1-k^{-1})^{\frac{1}{2}}. \quad . \quad . \quad . \quad . \quad (17)$$

Therefore from (7) we have

$$sg^{-1}=k^{-1}(1-k^{-1})^{-\frac{1}{2}}\sigma \quad . \quad . \quad . \quad . \quad (18)$$

and

$$tg^{-1}=k^{-1}(1-k^{-1})^{\frac{1}{2}}\tau, \quad . \quad . \quad . \quad . \quad (19)$$

where

$$\sigma=1{\cdot}25\, g^{-1}H_0/p \quad . \quad . \quad . \quad . \quad . \quad . \quad (20)$$

and

$$\tau=231\, g^{-1}Z^2/pH_0. \quad . \quad . \quad . \quad . \quad . \quad (21)$$

The quantities σ_1, τ_1, σ_2, and τ_2 can be calculated from the observed values of H_0 for each gas-mixture.

On substituting for sg^{-1} and tg^{-1} from equations (18) and (19), in the equations (15) and (16) they become the following :—

$$x=\sigma_1-\sigma_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (22)$$

$$y=\tau_1-\tau_2, \quad . \quad . \quad . \quad . \quad . \quad . \quad (23)$$

where

$$x\equiv k(1-k^{-1})^{\frac{1}{2}}(q_a-q_b) \quad . \quad . \quad . \quad . \quad (24)$$

and

$$y\equiv k(1-k^{-1})^{-\frac{1}{2}}(r_a-r_b). \quad . \quad . \quad . \quad . \quad (25)$$

In equations (22) and (23) the quantities x and y are known in terms of k ; σ_1, τ_1 are known in terms of ζ_1 ; and σ_2, τ_2 in terms of ζ_2. Thus for an assigned value of ζ_2 we may regard (22) and (23) as a pair of simultaneous equations in the two unknowns k and ζ_1, and solve them accordingly.

A convenient graphical method of solution is the following :—

By means of the known data for the gases A and B curves are drawn as in fig. 1 which give the values of q_a, r_a; q_b, r_b in terms of k. The quantities x and y defined by the formulæ (24) and (25) are then calculated by means of fig. 1 and the curve (x, y), shown in fig. 3, is drawn on transparent coordinate paper. Also the curve (k, y) is drawn on ordinary coordinate paper as in fig. 2. The observed pairs of values of σ and τ corresponding to given values of ζ are plotted as coordinates on ordinary

* V. A. Bailey, Phil. Mag. ix. pp. 566–7 (1930

Fig. 1.

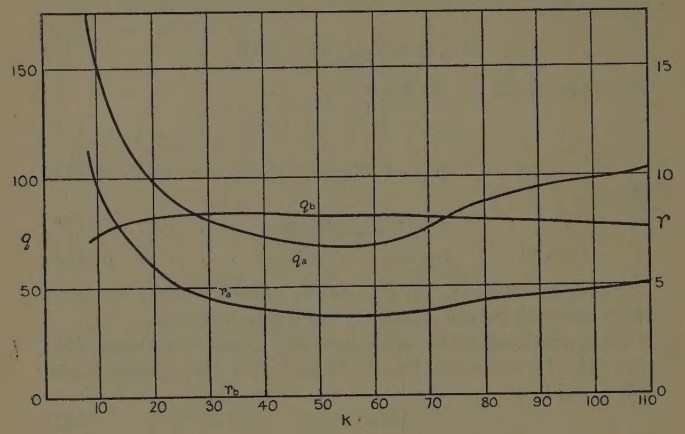
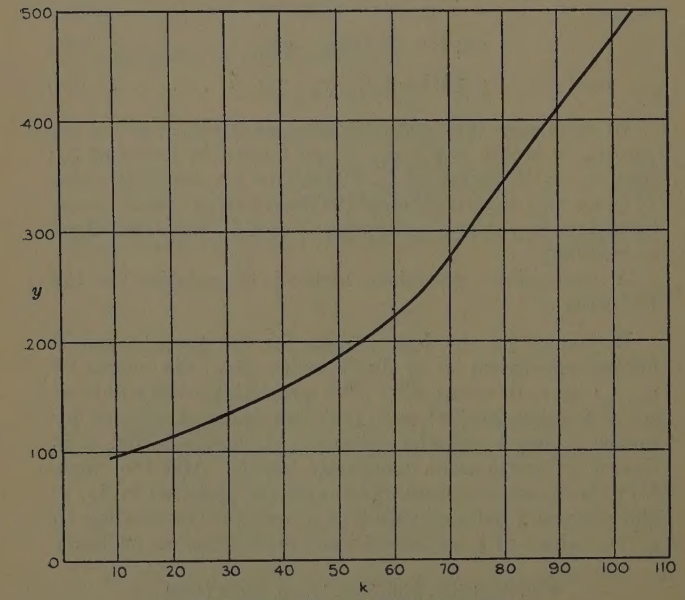


Fig. 2.

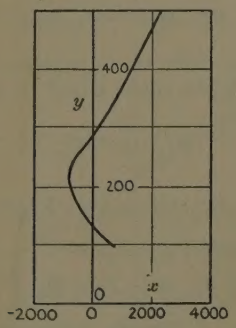


80 per cent. CO_2 and 80 per cent. He.

coordinate paper to the same scales as in fig. 3, and smooth curves are drawn through them as shown in fig. 4; the curve I. represents the observations made on the first mixture, and the curve II. those made on the second mixture.

Points P_1 and P_2 on the curves I. and II. corresponding to the same value of k are obtained by means of the following procedure, founded on equations (22) and (23). The transparent diagram (fig. 3) is placed on fig. 4, with the origin O at a selected point P_2, and the axes of co-ordinates parallel to the corresponding axes in fig. 4. The intersection of the curve (x, y) and the curve I. is the required point P_1 corresponding to P_2. The ordinate

Fig. 3.



80 per cent. CO_2 and 80 per cent. He.

y of the point P_1 considered as belonging to the transparent diagram (fig. 3) is read off and its value then determines on the diagram in fig. 2 the required value of k.

By means of equations (13) and (14) we can now obtain for the unknown gas X the corresponding values of the mean free path L_x and the mean proportion λ_x of its own energy which is lost by an electron at a collision.

An estimate of the relative accuracies of the new methods and the earlier ones may be made as follows.

The determination of k by means of the latter depends, among other things, on the quantity $R-S_2$, which, when many ions are present in the stream in the lower diffusion chamber, may easily be in error by 10 per cent. if S_2 and R are determinable within 2 per cent. But in

the new methods the application of the field H_0 increases the proportion of the stream which consists of free electrons by a factor which is easily shown to be greater than the ratio S_1S_2/R_e^2, where R_e is the distribution ratio which would be observed if the stream contained only free electrons. For if N and n represent respectively the number of ions and electrons passing through a specified slit per second, and if F is the proportion of the stream, passing through the slit, which consists of free electrons, then for the successive slits 0, 1, and 2 we have, respectively,

$$F_0=n_0/(N_0+n_0),$$

$$F_1=n_1/(N_1+n_1)=n_1F_0/S_1n_0=R_ee^{-\alpha c}F_0/S_1,$$

and $$F_2=R_ee^{-\alpha c}F_1/S_2.$$

Therefore $$F_2=R_e^2e^{-2\alpha c}F_0/S_1S_2.$$

When the magnetic field H_0 is present, each of the quantities R_e, S_1, and S_2 becomes equal to R, and the corresponding relation is

$$F_{2h}=e^{-2\alpha c}F_{0h}.$$

Therefore

$$F_{2h}/F_2=(S_1S_2/R_e^2).F_{0h}/F_0.$$

Clearly we must have $F_{0h}>F_0$, so

$$F_{2h}/F_2>S_1S_2/R_e^2.$$

For example, in a certain experiment the following values were obtained :—

$$S_1=\cdot232,\quad S_2=\cdot375,\quad R_e=\cdot195,\quad \text{and}\quad R=\cdot747.$$

Hence

$$F_{2h}/F_2>2\cdot3\quad \text{and}\quad R-S_2=\cdot372.$$

Thus the determination of H_0 depends on observations with a stream which has a proportion of free electrons at least 2·3 times as great as the proportion which exists during the determination of the quantity $R-S_2$. So the quantity H_0 may in general be determined more accurately than the quantity $R-S_2$, on which the accuracy of the earlier methods depends. This advantage is reinforced by the higher accuracy which, as mentioned before, results from requiring only one observation at each pressure.

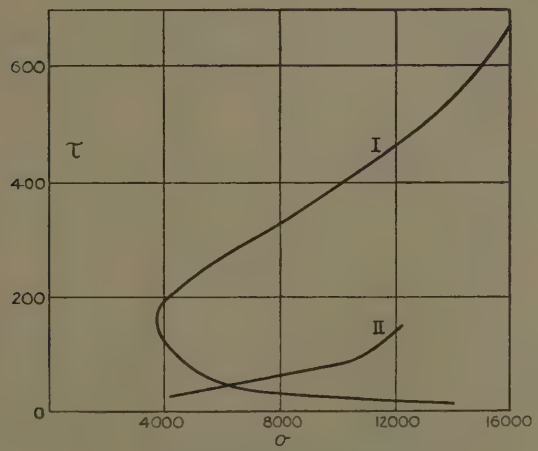
3. *Experimental Results.*

The three principal mixtures studied were the following :—

Mixture 1....	20 per cent. Cl_2+80 per cent. CO_2.
Mixture 2....	20 per cent. Cl_2+80 per cent. He.
Mixture 3....	40 per cent. Cl_2+60 per cent. CO_2.

The observed values of S_1 and S_2, with different electric intensities Z, magnetic intensities H, and pressures p, are given in Tables IV., V., and VI., which refer respectively

Fig. 4.



Curve I. = 20 per cent. Cl_2+80 per cent. CO_2.
,, II. = 20 per cent. Cl_2+80 per cent. He.

to the mixtures 1, 2, and 3. The values of σ and τ deduced from these observations are given in the same tables.

The curves I. and II. in fig. 4 represent the values of σ and τ given in Tables IV. and V. respectively. The auxiliary curves (k, y) and (x, y) for the pair of gases CO_2 and He are those already given in figs. 2 and 3.

By means of these curves values of k in terms of $\zeta(=Z/p)$ for the first mixture have been determined in the manner described in section 2 ; these values are given in the

TABLE IV.

Mixture 1.—20 per cent. Cl_2+80 per cent. CO_2.

Z.	p.	Z/p.	H.	S_1.	S_2.	$\sigma\times10^4$.	$\tau\times10^2$.	k.	$W\times10^{-6}$.	α/p.
4	·8	5	..	·226	·316	..	..	8‡	..	·18
6	1·2	,,	..	·406	·548					
2	·4	,,	*900*	..	·450	1·41	·138	..	0·6	
7·2	1·2	6	..	·396	·577	..	..	15¶	..	·22
4·8	·8	,,	*894*	..	·605	·70	·375	..	2·0	
5·6	·8	7	..	·352	·512	..	..	22‡	..	·082
8·4	1·2	,,	..	·454	·606					
8·4	1·2	,,	*1060*	..	·697	·55	·65	..	3·6	
9·6	1·2	8	*802*	..	·716	·42	1·11	29¶	5·6	
12	1·2	10	..	·232	·375	..	..	40‡	..	·048
8	·8	,,	..	·179	·315					
8	·8	,,	68·2	·231	·323	..	..	40§	..	·053
8	·8	,,	227	·454	·496					
8	·8	,,	*497*	..	·690	·385	1·86	40*	10·0	
12·8	·8	16	..	·180	·314	..	..	60§	..	·056
12·8	·8	,,	79·4	·238	·338					
8	·5	,,	*520*	..	·690	·65	2·86	62*	12·0	
8	·4	20	*532*	..	·690	·83	3·50	71*	12·0	
19·2	·8	24	79·5	·213	·298	..	..	..	..	·032
9·6	·4	,,	*670*	..	·717	1·04	4·03	76*	12·0	
25·6	·8	32	79·5	·238	·324	..	..	84§	..	·017
25·6	·8	,,	487	·499	·535					
12·8	·4	,,	*885*	..	·754	1·38	5·40	83*	12·1	
32	·8	40	..	·243	·284	..	..	92§	..	·00
32	·8	,,	431	·477	·479					
12	·3	,,	*787*	..	·747	1·64	7·10	..	14·0	
12	·25	,,	*716*	..	·747	1·80	9·32	108†	17·2	

The values of H_0 are shown in italics in the column under H.

* k from mixtures 1 and 2.
† ,, from mixtures 1 and 3.
‡ ,, by "original" method.
§ ,, by "magnetic" method.
¶ ,, interpolated from fig. 5.

ninth column of Table IV., and are represented by small open circles in fig. 5.

The results from mixtures 1 and 3 have been used similarly, and the values of k so derived for mixture 1 are shown in Table V. under the eighth column, and are represented in fig. 5 by means of small crosses.

TABLE V.

Mixture 2.—20 per cent. Cl_2+80 per cent. He.

Z.	p.	Z/p.	H_0.	S_2.	$\sigma\times10^{-4}$.	$\tau\times10^{-2}$.	k.	$W\times10^{-6}$.
2·0	·5	4	320	·450	·425	·272	40	3·7
2·4	·4	6	377	·482	·589	·427	54	4·6
2·8	·4	7	450	·510	·707	·502	61	4·8
3·2	·4	8	512	·534	·800	·578	67	5·1
4·0	·4	10	580	·576	·910	·800	73	5·7
3·0	·3	10	441	·523	·921	·790	73	5·7
3·6	·3	12	522	·558	1·07	·978	78	6·1
4·2	·3	14	538	·583	1·12	1·26	80	6·9
4·8	·3	16	590	·605	1·22	1·50	81	7·3

TABLE VI.

Mixture 3.—40 per cent. Cl_2+60 per cent. CO_2.

Z.	p.	Z/p.	H_0.	S_2.	$\sigma\times10^{-4}$.	$\tau\times10^{-2}$.	k.	$W\times10^{-6}$.
9·6	·4	24	720	·714	·561	1·85	74	11·4
11·2	·4	28	830	·738	·646	2·19	70	11·2
12·8	·4	32	984	·753	·769	2·40	79	10·8
12·0	·2	60	696	·747	1·09	6·00	108	17·8

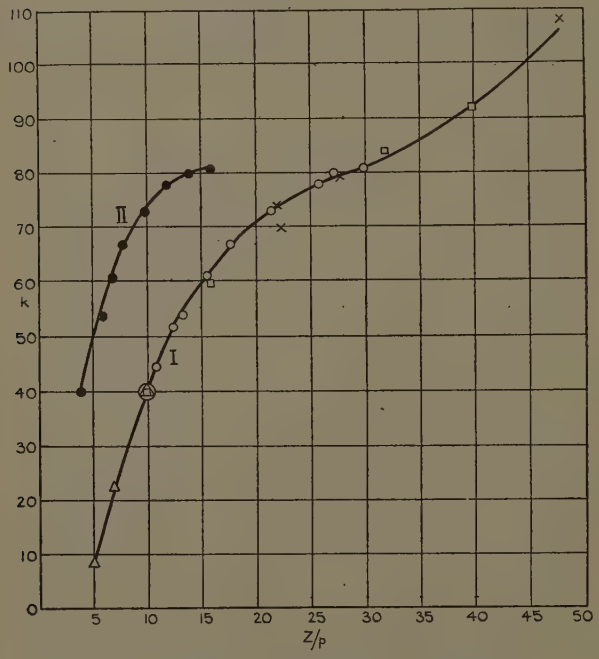
Values of k for mixture 1 have also been obtained from the data shown in Table IV. by means of the "original" and "magnetic" methods, and are indicated in fig. 5 respectively by small triangles and squares.

The smooth curves I. and II. in fig. 5, determined by means of these points, thus represent the values of k in terms of Z/p for mixtures 1 and 2 respectively.

The values of L and λ for pure Cl_2 in terms of the velocity u ($=1{\cdot}15\times10^7\sqrt{k}$), determined by means of the curves in figs. 1, 4, and 5 and the formulæ (13) and (14), are indicated similarly in figs. 6 and 7.

It will be seen that the results obtained by means of the three different methods are in excellent agreement.

Fig. 5.



Curve I. = k for mixture 1 : 20 per cent. Cl_2+80 per cent. CO_2.

„ II. = k for mixture 2 : 20 per cent. Cl_2+80 per cent. He.

Mixture 3 : 40 per cent. Cl_2+60 per cent. CO_2.

○ = k from mixtures 1 and 2.

× = k from mixtures 1 and 3.

▲ = k by " Original " Method.

□ = k by " Magnetic " Method.

● = k from mixtures 1 and 2.

A few observations of H_0 were also made on the following mixtures :—

Mixture 4.... $33\frac{1}{3}$ per cent. $Cl_2+66\frac{2}{3}$ per cent. CO_2.
Mixture 5.... 20 per cent. Cl_2+80 per cent. air,

and the values of L and λ in terms of k, deduced by combining these observations with those on mixture 1, were found to be in good agreement with the results shown in figs. 5, 6, and 7.

The values of W in the mixtures 1 and 2 corresponding to different values of Z/p are also given in Tables IV. and V., W being calculated by means of the formula

$$W=10^8(Z/H_0)\sqrt{k-1}.$$

The values of α/p may be calculated by means of the following formula * :

$$\alpha=\cdot 575\{\log_{10}R(Z/k)-\log_{10}a\},$$

where

$$a=S_1(R-S_2)/(R-S_1).$$

Such values are shown in the last column of Table IV.

If h_a and h_x are the probabilities of attachment of an electron in the gases A and X respectively (for a given value of k), it is easy to show that in the mixture

$$\alpha/p=(h_af_a/L_a+h_xg_a/L_x)u/W,$$

where u is the velocity of agitation and W is the drift velocity.

For CO_2 we have $h_a=0$, so with the help of (7) and (11) we obtain the formula

$$h_x=\cdot 037(\lambda_x+r_aL_x)k\alpha/Z. \quad . \quad . \quad . \quad . \quad (26)$$

The values of h for chlorine, calculated by means of (26), are represented by a curve in fig. 8.

4. *Values of k, W, and α/p in Chlorine.*

From the values of L, λ, and h in terms of u for chlorine we can derive the quantities W and α/p in terms of $\zeta(=Z/p)$ by means of the following formulæ :

$$W=\cdot 64u\lambda^{\frac{1}{2}},$$

$$\zeta=4\cdot 4\times 10^{-16}u^2\lambda^{\frac{1}{2}}/L,$$

and $$\alpha/p=1\cdot 57h/L\lambda^{\frac{1}{2}}.$$

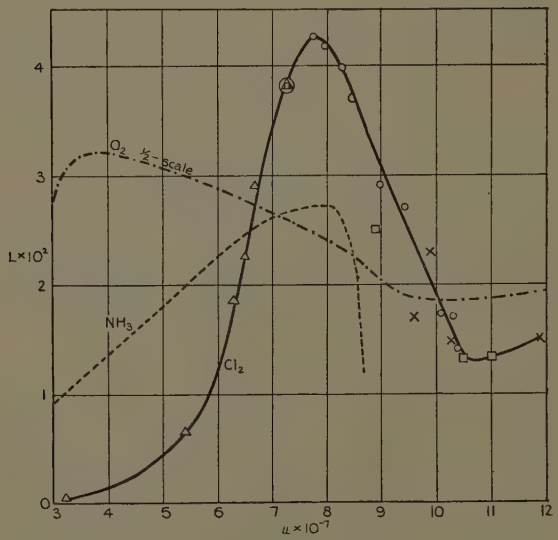
* *v.* V. A. Bailey, Phil. Mag. l. p. 842 (1925).

The quantities k, W, and α/p for electrons in chlorine are represented in terms of Z/p by the curves in fig. 9.

5. *The Variations of L, λ, and h with u in Chlorine.*

The quantities L, λ, and h for chlorine in terms of the velocity of agitation u are represented by curves in figs. 6, 7, and 8 respectively ; for comparison the corresponding curves for NH_3 and O_2* are given.

Fig. 6.



○ = L from mixtures 1 and 2.
× = L from mixtures 1 and 3.
△ = L by "Original" Method.
□ = L by "Magnetic" Method.

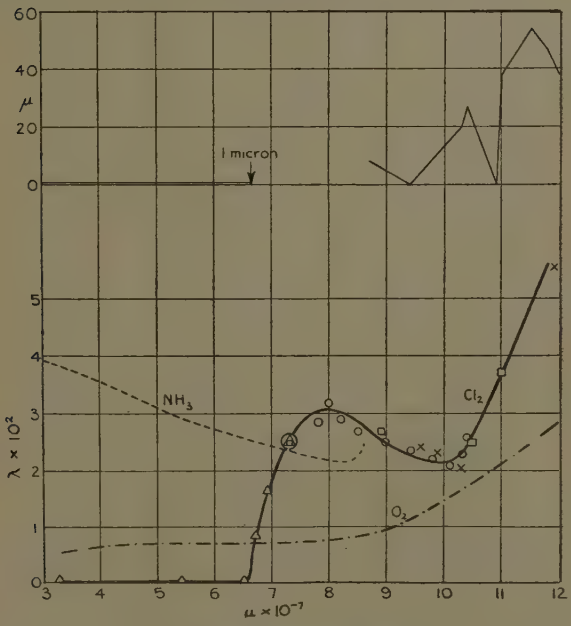
It will be seen from fig. 6 that as u ranges from $3{\cdot}25\times10^7$ to $11{\cdot}8\times10^7$ the mean free path L in chlorine rises from about $0{\cdot}05\times10^{-2}$ to a maximum value $4{\cdot}25\times10^{-2}$, and

* The values of h for oxygen are deduced from the values of α/p in air (Phil. Mag. l. p. 825 (1925)), the observations of W in air by Townsend and Tizard, and the values of L in oxygen obtained by Brose (Phil. Mag. l, p. 536 (1925)).

then diminishes to $1{\cdot}40\times10^{-2}$. Thus the mean free path in chlorine may change by the large factor 90.

Fig. 7 shows that as the velocity u increases from $3{\cdot}25\times10^{7}$ the proportion λ of energy lost at a collision of an electron with a molecule of chlorine increases from values less than $0{\cdot}1\times10^{-2}$ to a maximum value $3{\cdot}1\times10^{-2}$ at the velocity $8{\cdot}1\times10^{7}$, diminishes again to a minimum

Fig. 7.



○ = λ from mixtures 1 and 2.
× = λ from mixtures 1 and 3.
▲ = λ by "Original" Method,
□ = λ by "Magnetic" Method.

value $2{\cdot}1\times10^{-2}$ at a velocity of about 10×10^{7}, and then increases very rapidly to values exceeding 5×10^{-2}.

For comparison the optical absorption coefficient * μ for

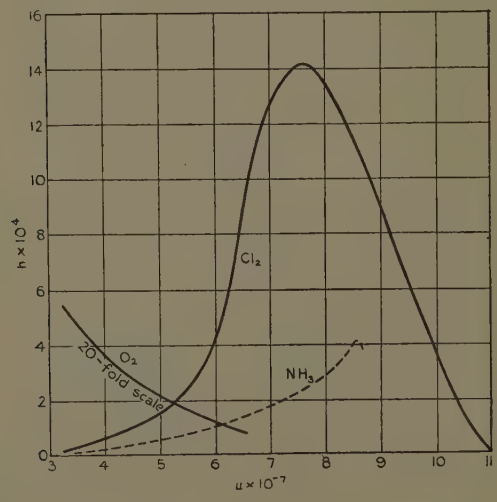
* *v.* Peskov, *J. Soc. Physic. Chim. St. Pet.* xlvii. (1913); Bayliss and Gibson, Phys. Rev. xliv. (1933); Halban and Siedentopf, *Zeits. f. Phys. Chem.* ciii. p. 71 (1922–23); and W. Burmeister, *Verh. d. Deut. Phys. Ges.* 1913, p. 589.

chlorine is also shown in fig. 7 plotted against the electronic velocity u equivalent to a given optical frequency ν.

It will be noticed that, roughly, small values of the fraction λ correspond to small values of μ and large values of λ correspond to large values of μ. The existing distribution of electronic velocities about the mean velocity precludes a more accurate correspondence between the curves for λ and u than occurs in the diagram.

It may be mentioned that these results were predicted in 1932, as the following quotation * shows :—. . . . since,

Fig. 8.



according to Burmeister, Cl_2 and Br_2 are transparent to wave-lengths greater than $1\,\mu$, we may expect low values of λ or velocities less than $6{\cdot}6 \times 10^7$. The fact that these gases are coloured makes it probable that large values of λ will be found for velocities between 7×10^7 and 12×10^7."

It is also interesting to note that the maximum value of λ occurring at the velocity $8{\cdot}1 \times 10^7$ appears to correspond to a weak maximum of the absorption coefficient μ which

* V. A. Bailey, Phil. Mag. xiii. p. 998 (1932).

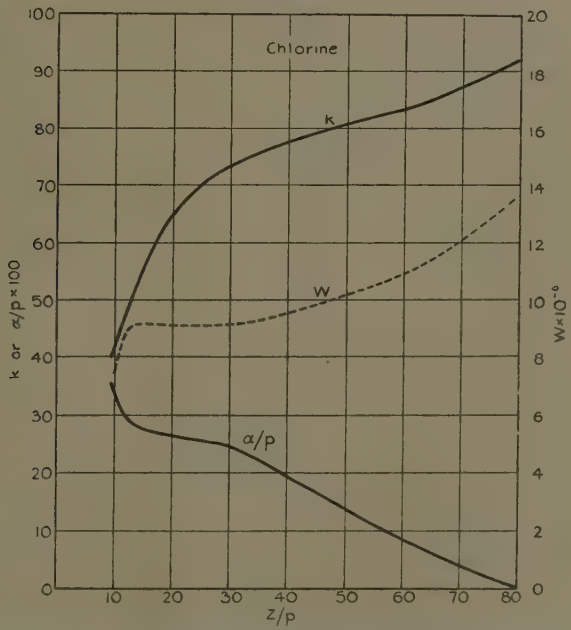
was found by Halban and Siedentopf at a wave-length equivalent to the electronic velocity $8{\cdot}2\times10^7$.

Fig. 8 shows that as u increases from $3{\cdot}25\times10^7$ to 11×10^7 h in chlorine increases from 10^{-5} to $1{\cdot}4\times10^{-3}$, and then diminishes to a small value.

This enormous change of h with u is comparable with the corresponding change in ammonia.

It will also be noticed that the variation of h with L for chlorine furnishes another example of the generalization,

Fig. 9.



previously published *, that the probability of attachment increases as the electron penetrates further into the molecule.

6. *General Discussion.*

The results of this investigation on chlorine have an interesting bearing on certain views, current among the

* V. A. Bailey and W. E. Duncanson, *loc. cit.*; V. A. Bailey and J. B. Rudd, *loc. cit.*; and V. A. Bailey and J. M. Somerville, Phil. Mag. xvii. p. 1169 (1934).

followers of J. Franck, about the collisions between electrons and molecules of gases, and so these views may be with advantage discussed here.

They attribute many of the phenomena connected with these collisions to the "electron-affinity," which is defined as the work done on an electron when it becomes attached to an atom or molecule. For example, Franck and Jordan * say: "Additional qualitative evidence of the electron-affinity of the halogens is provided by numerous facts; there may be mentioned .... the small mobility of negative ions in chlorine, the high resistance to breakdown of gases which contain free or combined halogens, the great influence on the discharge-potentials of small contaminations by halogens."

This quotation shows that in regard to the formation of negative ions they make the same error which Franck and his followers made in their earlier work on ionization and excitation by collisions of electrons, namely, they omit to consider the probability of happening of the given phenomenon.

Again, their reference to the sparking potential indicates that they consider that the ionization by the positive ions in halogens may be ignored as one of the factors determining the sparking potentials.

Another view, originally due to Franck and Hertz †, is as follows:—".... the collisions between electrons and gas molecules are the more elastic the less is the electron-affinity of the corresponding gas molecules."

The results of our experiments are in complete disagreement with these conclusions, for we find that the collisions between slow electrons and chlorine molecules are highly elastic, and more so than in hydrogen, in which no negative ions are appreciably formed. For example, between the velocities 3×10^7 and $5{\cdot}5\times10^7$ the proportion of energy λ lost at a collision with a molecule is less than 0·1 per cent. in chlorine and greater than 0·28 per cent. in hydrogen.

A similar mistake has been made by Franck and Hertz with regard to collisions of slow electrons with molecules of oxygen. These collisions were said to be non-elastic, and the electrons were said to form negative ions by becoming attached to the molecules of oxygen.

* Franck and Jordan, 'Anregung von Quantensprungen,' p. 763.

† Franck and Hertz, *Verh. d. Deut. Phys. Ges.* 1913, pp. 620 and 932.

If this were true the electrons in the Kennelly-Heaviside layer of the upper atmosphere would rapidly become attached to molecules and would cease to be effective in reflecting electromagnetic waves at night. According to the current theories the ordinary long distance radio-telephony would then be impossible. The original experiments * on the motions of electrons in air, which were made in 1908 and 1913 by the method designed by Townsend, showed that electrons make many collisions with molecules of oxygen without losing a large part of their energy or forming negative ions. The results of these experiments have provided the data required to explain the interaction of radio-waves † which has been recently observed in connexion with high power transmitting stations.

Wahlin ‡ has carried out experiments with chlorine and has been unable to observe any free electrons in the gas. He concludes from this that h for chlorine is greater than 5×10^{-4}. This is in disagreement with our results for the slower electrons, which give values for h of the order 10^{-5}.

It is evident that the erroneous views now current about the phenomenon of electron-attachment are in part due to the neglect of the possibility that the mean free path L and the probability of attachment h may vary considerably with the velocity of the electrons.

In conclusion, we desire to record our indebtedness to Mr. L. W. O. Martin, B.Sc., for preparing our pure gold chloride, to Messrs. G. C. Barnes, H. Taylor, and N. R. Wilson for the excellent construction of apparatus used in this investigation, and to the Colonial Sugar Refining Co., Ltd., and the Commonwealth and Accessories Co., Ltd., for supplying without cost carbon-dioxide snow and liquid air respectively.

Summary.

The motions of electrons in chlorine is studied by means of observations on chlorine and on different mixtures of chlorine with carbon dioxide or helium. The theory

* J. S. Townsend, Proc. Roy. Soc. A, lxxxi. p. 464 (1908); and J. S. Townsend and H. T. Tizard, Proc. Roy. Soc. A, lxxxviii. p. 336 (1913).
† V. A. Bailey and D. F. Martyn, Phil. Mag. xviii. pi. p. 369 (1934).
‡ Wahlin, Phys. Rev. xix. p. 173 (1922).

of a new method used is given in detail, and its advantages discussed. The values in chlorine of L the mean free path of an electron in the gas at 1 mm. pressure, λ the mean proportion of its own energy lost by an electron at a collision with a gas molecule, and h the probability of an electron becoming attached to the molecule with which it collides, deduced from the observations, are shown in terms of the velocity u by means of curves. The results obtained by means of three different methods are found to be in excellent agreement. The values of k the mean energy of agitation of an electron in terms of the mean energy of agitation of a molecule at 15° C., W the drift velocity of an electron in the direction of Z, and α/p the probability of attachment of an electron per unit length in the direction of the electric force at unit pressure, for electrons in chlorine, are also deduced, and shown in terms of Z/p by means of curves. A notable number of free electrons is observed in pure chlorine at pressures from 0·1 to 3·3 mm. and forces from 5 to 10 volts/cm.

It is found that L, λ, and h vary considerably with the electronic velocity u. There is a general correspondence between the values of λ and the optical absorption spectrum. Also the variation of h is similar to that of L.

The bearing of these results on certain published views about the motions of electrons in gases is also discussed.

LVIII. *Dipole Rotation in Solid Non-crystalline Materials.* *By* A. Gemant. (*Communication from the Engineering Laboratory, The University, Oxford* *.)

1. *Introduction.*

THE dipole theory of P. Debye [1] proved to be a very capable one for explaining the behaviour of dielectric constant and dielectric losses. Besides the layer-mechanism of Maxwell-Wagner [2] it accounts for the observed phenomena in a reasonably quantitative manner.

* Communicated by Prof. R. V. Southwell, M.A., F.R.S.

The exact theory refers to gases and liquids. Now unfortunately the most important insulators are solids, and the theory for those has not been developed satisfactorily until now. That is quite understandable, solids being more complicated than liquids owing to the greater rôle of molecular fields. Some crystalline bodies are dealt with, as, for instance, in the extended experiments of Errera[3]. There is also a preliminary theory of Debye[4] and another by Pauling concerning crystalline lattices.

However, a large class of real insulating materials are not crystalline. Glass, rubber, paraffin wax, bakelite, to mention a few examples, are polyphasic systems containing some components in a micro-crystalline form, others in the amorphous state. It would be of value therefore to investigate how the dipole theory can be applied to such solid, not purely crystalline, materials.

As a rigorous theory seems to be by far too complicated, the paper deals with a rather simple extension of the dipole theory.

The amorphous state can be defined as a liquid one having an extremely high viscosity. If this were the case, then the Debye theory could be applied to such bodies without further notice. One simply has to put a high value for the viscosity and correspondingly for the time constant. However, careful measurements of viscosity on very viscous liquids reveal the existence of a certain elasticity in such materials. This has been shown for colloidal watery solutions [5], and the author has succeeded in showing the same for oils[6]. It seems, therefore, that the introduction of elasticity, coexisting with viscosity, is a useful basis on which to describe amorphous bodies. This description is clearly far from complete, but it may be regarded as a suitable second approximation.

In the following pages such kind of non-crystalline materials will be considered. The purpose of the paper is to show how the dipole theory has to be extended, if the material exhibits a finite elasticity.

It has been shown by Weissenberg[7] that the frictional losses in such a material decrease with increasing frequency. It might well be expected, therefore, that this behaviour would affect the dipole losses in a dielectric in a rather pronounced manner. As the following deduction shows this is not the case. There is no marked influence of

elasticity on dipole rotation, and the order of size of the characteristic data remains unaltered. The use of the Debye theory in such materials is fully justified.

2. *Specification of the Model.*

We adopt the following picture for the structure of dielectric under consideration. The dipoles are in a state of thermal agitation which tends to maintain a random distribution. The electric field tending to orient the dipoles has to work against this thermal agitation. During their motion the dipoles "bump" neighbouring molecules, thus transferring a part of their momentum of motion, a phenomenon which can be described by assuming a rotation in a viscous medium. This viscosity is frequently different from the macroscopic viscosity, especially if the motion of the dipoles takes place in the interspaces of a certain microstructure, consisting of a crystalline phase embedded in the coexisting liquid phase, which may increase the macroscopic viscosity to a great extent. So far the original equations of Debye govern the rotation of dipoles.

But there is an elastic resistance to the rotation of dipoles. The material has a certain elasticity modulus E, and the dipoles have to overcome this elasticity as well as the thermal agitation. But this elasticity is not a perfect one ; it is a relaxing type of elasticity. We make use here of the conception used primarily by Maxwell. The materials under consideration, not being real crystals, do not keep deformation for an infinite time, as real crystals would. They relax rapidly, since their structure is capable of viscous flow and reorientation. The lattice is not an absolute one ; once deranged, the elastic restraint lasts only for a time, then relaxes, the molecules exhibiting a certain viscous flow and forming a new lattice. If the viscosity of the medium is η, the time constant τ_0 of the elastic relaxation is

$$\tau_0 = \frac{\eta}{E}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

We may now calculate the response of dipoles according to the second mechanism. If the result can be obtained in form of a complex impedance, all one has to do is to add this to the impedance which can be derived from

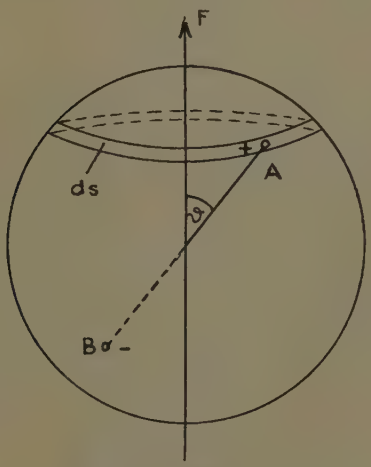
Debye's theory, in order to get the real response of dipoles according to both mechanisms acting together.

The method just sketched is not absolutely rigorous, as the two mechanisms are not quite independent. But the model itself is only an approximation, and there is another uncertainty related with the value of τ_0 (referred to later). In view of these facts the approximate method of calculation can be considered as justified.

3. *Rotation of Dipoles in an Elasto-Viscous Medium.*

The first step consists in determining the response of dipoles to an alternating electric field in a medium having

Fig. 1.



Dipole in the unit sphere.

elasticity and viscosity, but showing no thermal agitation. In other words, we look for the conditions near the absolute zero point of temperature.

Let us consider a unit sphere (fig. 1), the vertical axis denoting the direction of the external field F, the upward direction being positive. AB is the direction of the dipole under consideration, its moment being μ. The angle between F and μ is ϑ. The alternating field is then denoted by $F_0 e^{i\omega t}$ (F_0 is the amplitude, ω the frequency times 2π, and t the time).

There are two forces acting on the dipoles, the electric couple and the elastic forces raised by the rotation. A field F exercises an angular moment M:

$$M = -F\mu \sin \vartheta.$$

M is represented with minus sign, as it tends to decrease the angle ϑ. The moment due to an alternating field is

$$M = -F_0\mu \sin \vartheta e^{i\omega t}. \quad . \quad . \quad . \quad . \quad . \quad (2)$$

The result of such a torque will be an oscillation of the dipole in the plane determined by F and μ. As the field is a sinusoidal one, the oscillation is supposed to be sinusoidal also, that is,

$$\vartheta = \vartheta_0 e^{i\omega t}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (3)$$

Each infinitesimal deflexion raises an elastic counter-force. Let us consider a deflexion

$$d\vartheta = iw\vartheta_0 e^{i\omega t} dt. \quad . \quad . \quad . \quad . \quad . \quad (3\,a)$$

If there were no finite viscosity, the elastic couple would be

$$dN' = -\gamma d\vartheta. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (4)$$

The quantity γ is evidently a function of the size and shape of the dipole and the modulus E. If the dipole is roughly a rigid sphere of radius r, then γ is a function of r and E. The author has not succeeded in finding in the literature the function $\gamma(r, E)$, so this question must be left open.

The existence of viscosity will cause a relaxation of the couple dN; its value after a certain time t is, according to (1),

$$dN = -\gamma e^{-\frac{t}{\tau_0}} d\vartheta. \quad . \quad . \quad . \quad . \quad . \quad (4a)$$

The total couple exercised on the dipole at a given time $t=0$ will be a superposition of all the elementary quantities $(4\,a)$, thus

$$N = -\gamma \int e^{-\frac{t}{\tau_0}} d\vartheta. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

As all the times t under consideration are negative, the sign of the exponential must be changed. Placing $(3a)$ in (5),

$$N = -i\omega\gamma\vartheta_0 \int_{-\infty}^{0} e^{\frac{t}{\tau_0}} e^{i\omega t} dt. \quad . \quad . \quad . \quad . \quad (6)$$

This gives

$$N=-i\omega\gamma\vartheta_0\frac{1}{\frac{1}{\tau_0}+i\omega},$$

or
$$N=-i\gamma\vartheta_0\frac{\omega\tau_0}{1+i\omega\tau_0}. \quad . \quad . \quad . \quad . \quad . \quad (7)$$

This expression is the complex amplitude of the elastic torque. Equilibrium is obtained if the sum of (7) and of the amplitude of (2) is zero, so that

$$F_0\mu\sin\vartheta+i\gamma\vartheta_0\frac{\omega\tau_0}{1+i\omega\tau_0}=0.$$

This equation is fulfilled if

$$\vartheta_0=-\frac{F_0\mu\sin\vartheta}{\gamma}\left(1-\frac{i}{w\tau_0}\right). \quad . \quad . \quad . \quad . \quad (8)$$

Equation (8) is the result of the calculation ; it gives the amplitude of dipole rotation as a function of the field. There is one component in phase with the field and another in advance quadrature.

4. *Dipole Polarization in an Elasto-Viscous Medium.*

The next step is the calculation of the polarization per unit volume, P, due to dipole rotation.

Each dipole contributes to P. The dipole in the direction AB (fig. 1) exhibits an additional electric moment in the direction of the field F:

$$dP=-\mu\vartheta_0\sin\vartheta. \quad . \quad . \quad . \quad . \quad . \quad (9)$$

This is shown better by fig. 2.

AB is here a dipole having charges $\pm e$ and length l. The moment in the direction F is evidently $\mu\cos\vartheta$. Through the oscillation with amplitude ϑ_0 the additional moment in the direction F becomes 2CDe. Now AC is

$$-\frac{\vartheta_0 l}{2} \quad \text{and} \quad CD=-\frac{\vartheta_0 l\sin\vartheta}{2}.$$

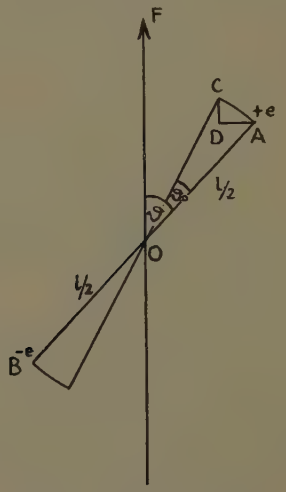
The additional moment is therefore

$$dP=2CDe=-\vartheta_0 le\sin\vartheta=-\mu\vartheta_0\sin\vartheta,$$

as in (9).

The total value P can be obtained by integrating over every dipole of the volume unit. The distribution of the dipoles pointing to different spots on the unit sphere (fig. 1) is a uniform one. If the total number of dipoles in the cm.^{3} is n, then the number pointing to a certain surface element ds on the unit sphere is equal to $\frac{ds.n}{4\pi}$. Consider a ring element ds comprising all the directions

Fig. 2.



Additional moment of a dipole.

having an angle ϑ with F. Then $ds = 2\pi \sin \vartheta . d\vartheta$, and the number of dipoles in it is

$$\frac{n \sin \vartheta . d\vartheta}{2}.$$

The corresponding polarization is therefore obtained by multiplying this number by (9); that is,

$$dP = -\tfrac{1}{2} n\mu\vartheta_0 \sin^2 \vartheta . d\vartheta.$$

This has to be integrated over the whole surface, including all possible directions ϑ.

$$P = \frac{F_0 n\mu^2}{2\gamma}\left(1 - \frac{i}{\omega\tau_0}\right)\int^{\pi} \sin^3 \vartheta . d\vartheta. \quad . \quad . \quad (10)$$

The value of the definite integral being 4/3,

$$P=\frac{2F_0 n\mu^2}{3\gamma}\left(1-\frac{i}{\omega\tau_0}\right). \quad . \quad . \quad . \quad . \quad . \quad (11)$$

Now P and F_0 are related by the general equation

$$P=\alpha F_0,$$

where α denotes the polarizability ; hence

$$\alpha=\frac{2n\mu^2}{3\gamma}\left(1-\frac{i}{\omega\tau_0}\right). \quad . \quad . \quad . \quad . \quad . \quad (12)$$

It is very easy to evaluate from α the dielectric constant ϵ and the loss angle $tg\delta$. One has to make use of the Clausius-Mossotti equation

$$\frac{\epsilon-1}{4\pi}=\alpha,$$

which will be used in the following for the sake of simplicity instead of the more correct Lorentz equation

$$\frac{3}{4\pi}\frac{\epsilon-1}{\epsilon+2}=\alpha.$$

This is allowable if ϵ is of the order 1 or 2, which is the case for good dielectrics. Hence

$$\frac{\epsilon-1}{4\pi}=\frac{2n\mu^2}{3\gamma}\left(1-\frac{i}{\omega\tau_0}\right). \quad . \quad . \quad . \quad (13)$$

On separating ϵ according to

$$\epsilon=\epsilon'-i\epsilon''$$

where ϵ' = the equivalent dielectric constant and $\epsilon''/\epsilon'=tg\delta$ (see [8]), (13) gives

$$\epsilon'=1+\frac{8\pi n\mu^2}{3\gamma} \quad . \quad . \quad . \quad . \quad . \quad . \quad (14)$$

and

$$tg\delta=\frac{1-\frac{1}{\epsilon'}}{\omega\tau_0}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (15)$$

which is equivalent to a parallel conductivity

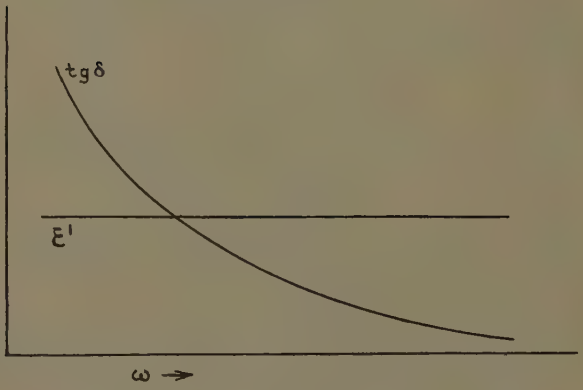
$$\sigma=\frac{2n\mu^2}{3\gamma\tau_0} \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16)$$

(14) and (16) are the main results of the calculation. They show that the model dielectric pictured in Section 2

is really equivalent to a dielectric possessing a dielectric constant given by (14) and a parallel conductivity given by (16). Such a circuit must have a power factor, which is inversely proportional to the frequency, as shown by (15). The behaviour of ϵ' and $tg\delta$ is shown diagrammatically in fig. 3.

Equation (16) can be transformed in the following manner. Let us introduce the torque exercised on a sphere rotating in a viscous medium, and designate this

Fig. 3.



Dielectric constant and loss angle in elasto-viscous medium.

torque ζ, referred to unity of angular velocity. The corresponding equation of Stokes says

$$\zeta = 8\pi r^3 \eta. \quad . \quad . \quad . \quad . \quad . \quad . \quad (17)$$

As Debye[9] points out, the same equation cannot hold for dipoles, as it was deduced for spheres moving in a *continuous* medium. It remains doubtful what value is to be attached to r, the radius of the equivalent sphere, and especially what is meant by the value of the "viscosity," the latter not being the same as the macroscopic viscosity, even in a pure liquid. However, the dimensions of equation (17) are correct.

As to the similar quantity γ, its value is known even less certainly than that of ζ, as already mentioned; but

the dimensions of r and E must be the same as in (17). We can therefore write

$$\gamma = 8\pi c r^3 E. \quad . \quad . \quad . \quad . \quad . \quad . \quad (18)$$

Dividing (17) by (18)

$$\frac{\zeta}{\gamma} = \frac{\eta}{cE} = \frac{\tau_0}{c}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (19)$$

or

$$\gamma\tau_0 = c\zeta. \quad . \quad . \quad . \quad . \quad . \quad . \quad (19\,a)$$

Hence (16) can be written as

$$\sigma = \frac{2n\mu^2}{3c\zeta}. \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (16\,a)$$

This expression shows that the loss is given simply by the value of the viscosity, having nothing to do with the elasticity. This latter only adds a term to the dielectric constant, according to (14). The limiting case of a normal liquid is characterized by $\gamma = \infty$, the polarization term due to dipoles vanishes, the conductivity is unchanged, provided η keeps constant.

It may be that an experimental check of formulæ (14) and (15) would be possible at very low temperatures not too far from the absolute zero, for a material in the non-crystalline state.

5. *Polarization in an Elastic Medium at Finite Temperature.*

According to the method oulined in Section 2, the result obtained has to be combined with the equations of Debye. A simple addition of this kind is, as already stated, not rigorous, but is sufficient to get the required information.

It has to be decided which kind of addition is appropriate. The dipoles have to work during their rotation against thermal agitation and elasticity. This means the impedances are in series, the velocity being the same for both. The polarizability is evidently the reciprocal of an impedance. The reciprocals of the polarizabilities have therefore to be added. One of them is given by (12), which may be now denoted by α_e (elasticity term). The corresponding formula of Debye is a thermal term

$$\alpha_t = \frac{n\mu^2}{3kT}\left(\frac{1}{1+i\omega\tau}\right), \quad . \quad . \quad . \quad . \quad . \quad (20)$$

where k=Boltzmann constant, T=absolute temperature, and

$$\tau=\frac{\zeta}{2k\mathrm{T}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad (20\,a)$$

the time constant of thermal agitation. The reciprocal of the sum of both reciprocals gives the total polarizability α:

$$\alpha=\frac{1}{\frac{1}{\alpha_e}+\frac{1}{\alpha_t}}.$$

Putting (12) and (20) in this, gives

$$\alpha=\frac{n\mu^2}{3}\cdot\frac{1}{\frac{\gamma}{2}\frac{\omega\tau_0}{\omega\tau_0-i}+k\mathrm{T}(1+i\omega\tau)}. \quad . \quad . \quad (21)$$

For further evaluation let us take $c=1$ in equation (19 a), in order to avoid undue complication. On eliminating γ by the said equation (21) may be brought to the normal form and gives

$$\alpha=\frac{n\mu^2}{3k\mathrm{T}}\frac{1+\omega^2\tau_0(\tau+\tau_0)-i\omega\tau(2+\omega^2{\tau_0}^2)}{1+\omega^2(4\tau^2+2\tau\tau_0+{\tau_0}^2)+\omega^4\tau^2{\tau_0}^2}. \quad . \quad (22)$$

This equation shows clearly the extent to which the adopted method of adding the polarizations is faulty. On putting $\tau_0=0$ (normal liquids) we get again equation (20), but the value of τ is doubled. This is some measure of the uncertainty in equation (22). The reason for this is evident: since the viscosity effect has been considered twice, τ becomes doubled.

In evaluating ϵ' and $tg\delta$ from (22) and the Clausius-Mossotti relation, the values of dielectric constant for d.c., and for infinite frequency, ϵ_0 and ϵ_∞ may be introduced, according to Debye. Thus

$$\epsilon_0-\epsilon_\infty=\frac{4\pi n\mu^2}{3k\mathrm{T}},$$

this difference arising from dipole polarization; ϵ_∞ accounts for the so-called electronic and atomic polarization. This leads to the final result for the dielectric constant

$$\epsilon'=\epsilon_\infty+\frac{1+\omega^2\tau_0(\tau+\tau_0)}{1+\omega^2(4\tau^2+2\tau\tau_0+{\tau_0}^2)+\omega^4\tau^2{\tau_0}^2}(\epsilon_0-\epsilon_\infty), \quad (23)$$

and for the loss angle

$$tg\delta = \frac{\omega\tau(2+\omega^2\tau_0^2)(\epsilon_0-\epsilon_\infty)}{(1+\omega^2\tau_0(\tau+\tau_0))\epsilon_0+\omega^2(4\tau^2+\tau\tau_0+\omega^2\tau^2\tau_0^2)\epsilon_\infty}. \quad (24)$$

with the uncertainty just mentioned. The two last equations are, of course, not valid for the neighbourhood of T=0, as in that case (22) leads back (approximately) to (12).

It is easy to show that (24) behaves very similarly to the original Debye equation

$$tg\delta = \frac{\omega\tau(\epsilon_0-\epsilon_\infty)}{\epsilon_0+\omega^2\tau^2\epsilon_\infty}. \quad . \quad . \quad . \quad . \quad . \quad (25)$$

So long as $\tau_0<\tau$ the difference between (24) and (25) is only of second order, as direct comparison shows. But when $\tau_0>\tau$, then different orders of ω have to be considered. So long as $\omega<\frac{1}{\tau_0}$ (low frequencies), (24) degenerates into

$$tg\delta = \frac{\omega\tau(\epsilon_0-\epsilon_\infty)}{\epsilon_0}$$

exactly as (25). When $\omega>\frac{1}{\tau_0}$, but $<\frac{1}{\sqrt{\tau\tau_0}}$, (24) degenerates into

$$tg\delta = \frac{\omega^3\tau\tau_0^2(\epsilon_0-\epsilon_\infty)}{\omega^2\tau_0^2\epsilon_0},$$

which is still identical with the foregoing formula. When $\omega>\frac{1}{\sqrt{\tau\tau_0}}$, (24) degenerates into

$$tg\delta = \frac{\omega^3\tau\tau_0^2(\epsilon_0-\epsilon_\infty)}{\omega^2\tau_0^2\epsilon_0+\omega^4\tau^2\tau_0^2\epsilon_\infty},$$

which is identical with (25). Exactly the same can be shown for the behaviour of the dielectric constant.

The small differences in any case can be partly accounted for in the uncertainty just referred to and have therefore no significance. The original equations of the dipole theory in liquids are therefore valid in amorphous solid materials. The physical reason for this somewhat paradoxical result is, that even for finite values of γ, representing a pronounced elastic resistance, there is a leak

acting parallel to it. This leak is originated by the viscous relaxation of elasticity and is of the same order as the thermal dipole loss, both phenomena being governed by the same viscosity coefficient.

6. *Summary.*

It is important to know whether the Debye theory of dipole rotation, originally developed for gases and liquids, can be used for solid materials of the amorphous, non purely crystalline type (paraffin, glass, etc.). Such materials are here considered as possessing both a finite value of viscosity and a certain elasticity capable of relaxation. The original theory is extended under this assumption. It turns out that the equations relating dielectric constant and loss angle with frequency, temperature and the characteristic dipole data are but slightly affected by a finite elasticity. The position of the anomalous dispersion region as well as the height of the absorption are unaltered. The application of the dipole theory to such solids is therefore justified.

The author is much indebted to Prof. R. V. Southwell, F.R.S., for facilities placed at his disposal in the Engineering Laboratory at Oxford, and to Metropolitan-Vickers Electric Co. Ltd., Manchester, for a grant enabling him to carry out this investigation.

Literature.

(1) P. Debye, ' Polar Molecules,' Chem. Cat. Comp. New York, 1929.
(2) A. Gemant, " Liquid Dielectrics." New York : Wiley, 1933, p. 84.
(3) J. Errera and H. Sack, ' Dipole Moments,' Disc. held by Faraday Soc. London : Gurney & Jackson, 1934 p. 687.
(4) P. Debye, ' Polar Molecules,' §21 ; L. Pauling, Phys. Rev. xxxvi. p. 430 (1930).
(5) R. Eisenschitz, *Koll. Zeits.* lxiv. p. 184 (1933) ; R. N. Schofield, ' Physics,' iv. p. 122 (1933) ; W. Philippoff, *Phys. Zeits.* xxxv. p. 884 (1934).
(6) A. Gemant, *Viskosität u. Fliessfestigkeit.* Berliner Akad. Berichte, 1932.
(7) K. Weissenberg, *Abhandl. der Berliner Akad.* 1932.
(8) A. Gemant, ' Elektrophysik d. Isolierstoffe.' Berlin : Springer, 1930, p. 10.
(9) P. Debye, ' Dipole Moments,' p. 679.

LIX. *Note on the Interrelation of the Equilibrium Nuclear Distance with other Molecular Constants for Diatomic Molecules.* *By* R. A. Newing, *A.R.C.S., B.Sc., Dept. of Applied Mathematics, University of Liverpool* *.

Summary.

Certain data from band-spectra are shown to lead to a general relation of the form $r_e = r_e(\omega_e, x_e, D_e, \mu)$, between the nuclear distance, r_e, and certain other molecular constants. Empirical relations have been set up in the form $r_e = r_e(\omega_e)$, and $r_e = r_e(\omega_e, \mu)$, and are therefore of a less general type. To establish the empirical relations on a theoretical basis it is necessary to carry out an investigation into the general properties of the potential curves of diatomic molecules. Certain suggestions are made as to the type of procedure that may prove sufficient for our purpose, but the detailed analysis will appear in a subsequent paper.

From a study of numerical data obtained from band-spectra there has been indication of the existence of a relation between the equilibrium nuclear distance, r_e, and certain other molecular constants. Birge †, and Mecke ‡, proposed the law $r_e^2\omega_e = \text{constant}$, for all states of a given molecule, $c\omega_e$ being the vibration frequency for infinitesimal amplitudes. Morse § proposed $r_e^3\omega_e = \text{constant}$, for a large class of molecules. Morse's law has recently been modified by Clark ‖, and by Badger ¶, who proposed $r_e^3\omega_e\sqrt{n} = k - k'$, and $\omega_e^2\mu(r_e - d_{ij})^3 = \text{constant}$, respectively, where k is a constant for a given molecular period, k' a small correction factor for ionized molecules, and d_{ij} is a constant for diatomic molecules made up of one element of the ith row and one of the jth row of the periodic system. In view of the empirical evidence that has been produced it is interesting to look for a theoretical basis for relations of this type.

* Communicated by the Author.

† R. T. Birge, Phys. Rev. xxv. p. 240 (1925).

‡ R. Mecke, *Zeits. f. Phys.* xxxii. p. 823 (1925).

§ P. M. Morse, Phys. Rev. xxxiv. p. 57 (1929).

‖ C. H. D. Clark, Phil. Mag. xviii. p. 459 (1934); 'Nature,' cxxxiii. p. 873 (1934).

¶ R. M. Badger, J. Chem. Phys. ii. p. 128 (1934).

§1. The wave equation for the nuclear motion of a diatomic molecule is

$$\nabla^2\psi+(8\pi^2\mu/h^2)[W-U(r)]\psi=0,$$

where μ is the reduced mass of the nuclei, W the vibration energy, and U(r) the potential energy of the system, calculated by considering the two nuclei as fixed at a distance r apart. Assuming $\psi=\Phi(\phi)\Theta(\theta)R(r)/r$, we have for R

$$\frac{d^2R}{dr^2}+\frac{j(j+1)}{r}R+\frac{8\pi^2\mu}{h^2}[W-U(r)]R=0, \quad . \quad (1)$$

$$j=0, 1, 2, \ldots$$

Now U(r) is a complicated function of r and the electronic quantum numbers, and is not known accurately. To calculate the theoretical vibration states of a molecule it is therefore necessary to assume some form U(r ; α_1, α_2..) of U, α_1, α_2, . . ., being parameters to be adjusted to give results in agreement with observation. Kratzer * proposed that in the neighbourhood of $r=r_e$, U(r) could be written as

$$E_e+a_2[\tfrac{1}{2}-r_e/r+r_e^2/2r^2-a_3\xi^3-a_4\xi^4 \ldots], \quad \xi=(r-r_e)/r_e,$$

E_e being the minimum energy at r_e. This has been rewritten by Fues† in the form $E_e+b_2\xi^2+b_3\xi^3+b_4\xi^4 \ldots$. Using these expressions for U(r), W may be deduced from (1), using perturbation methods, in the form

$$W_e=-D_e+ch\omega_e[(n+\tfrac{1}{2})-x_e(n+\tfrac{1}{2})^2+y_e(n+\tfrac{1}{2})^3+ \ldots .] \\ +\text{rotation terms}, \quad (2)$$

ω_e, x_e, y_e, ... being functions of μ, and of parameters occurring in the assumed potential function. This expression for W can be fitted well with deductions from band-spectra ; the constants ω_e, x_e, y_e, . . . , may be taken as known, and the parameters may then be calculated. Now these potential functions, valid in the neighbourhood of r_e, may be considered to be the expansion about this point of the actual potential function. It will then be expected that the parameters α_1, α_2, . . ., will not be independent, and therefore the functions as written will be too general. This has also been indicated by Morse

* Kratzer, *Zeits. f. Phys.* iii. p. 289 (1920).

† Fues, *Ann. d. Phys.* lxxx. p. 367, and lxxxi. p. 218 (1926).

on the grounds that the expression for W obtained contains no indication of the observed fact that the constants y_e, ... are very much smaller than ω_e and x_e. This result will follow from a less general function obtained by imposing a relation between the parameters. Morse proposed the function $E_e+D_e(1-e^{-ax})^2$, $x=r-r_e$, containing the three parameters a, r_e, D_e, D_e being the dissociation energy, and obtained an expression for W of the above form, with y_e, and all succeeding coefficients zero.

Taking for simplicity the state of pure vibration, $j=0$, we have for a general three parameter potential function

$$R''+(8\pi^2\mu/h^2)[W-U(r, D_e, r_e, a)]R=0. \quad . \quad . \quad (3)$$

U must be infinite at $r=0$, tend to E_e+D_e as r tends to infinity, and have a minimum value, E_e, at $r=r_e$. The condition that R is to be finite at the two boundary points, these being in general singular points of the differential equation, imposes a set of discrete values $W(n)$ on W, which we may suppose to be expressed in the form of (2). In this case ω_e, x_e, y_e, ... will appear as functions of the constants occurring in (3),

$$\omega_e=\omega_e(\mu, r_e, D_e, a), \quad x_e=x_e(\mu, r_e, D_e, a), \ldots .$$

The first relation, expressing ω_e in terms of r_e and other molecular constants, can be obtained, of course, by expanding U about r_e and equating the coefficient of $(r-r_e)^2$ to $2\pi^2\mu\omega_e^2$, but as we are looking for a relation between experimentally observed quantities, we eliminate the parameter, a, using the second relation obtained from the wave equation. We shall now expect relations of the form $r_e=r_e(\omega_e, x_e, D_e, \mu)$. Now Morse's function is of the form $U(r\,;\, D_e, r_e, a)$ and will be expected to provide results of this type, but it is found that r_e does not appear in his expressions for the experimental constants ω_e and x_e. This will be shown to arise from the fact that his potential function is finite at $r=0$.

§ 2. If it be supposed that the energy of the system is zero for infinite separation of the nuclei, $E_e=-D_e$, and with Morse's function equation (3) becomes

$$\frac{d^2R}{dx^2}+(8\pi^2\mu/h^2)[W-D_e e^{-2ax}+2D_e e^{-ax}]R=0.$$

This equation has no singularity at $r=0$, and to obtain eigen values, Morse had to introduce the range $-\infty \leq r \leq \infty$. This can be justified as an approximation to the physical problem, but with the modified interval, r_e does not appear in the differential system, and we thus lose the possibility of obtaining a relation of the type for which we are looking. It should be possible to obtain eigenwerte, using the correct interval $0 \leq r \leq \infty$, if the extra condition, $\psi(0)=0$, is imposed. This possibility has been investigated, but it has not been found possible to find a simple condition that will ensure that R is finite at the other boundary. We have therefore proceeded so to modify $U(r)$ that it becomes infinite at $r=0$. Consider the function

$$U(r)=-D_e+D_e\phi(r)f(r),$$

$$\phi(r)=(1-e^{-ax})^2.$$

If this is to be a suitable modification, $f(0)$ must be infinite, and ϕf must have a minimum at the minimum, $r=r_e$, of ϕ. The latter condition will be seen to be satisfied if $f(r_e)$ is finite and positive, and $f'(r_e)$ and $f''(r_e)$ are both finite. For large values of r, $f(r)$ must tend to unity. A function satisfying all these conditions, and such that $U(r)$ has only one minimum in $0 \leq r \leq \infty$, is

$$f(r)=[e^{ar_e}/(e^{-ar_e}-e^{-ax})]^2.$$

If therefore we write

$$U(r)=-D_e+D_e\beta^2[(1-y)/(\beta-y)]^2, \quad y_e=e^{-ax}, \quad \beta=e^{ar_e},$$

then this function may be taken as a suitable potential function. For a given molecule the parameter a will not have the same value as that occurring in Morse's function, but will be chosen to give the best agreement with experiment, and by such a choice $U(r)$ will be expected to conform closely to the actual potential curve, and, except in the neighbourhood of $r=0$, to the Morse curve. With $U(r)$ of this form equation (3) becomes

$$R''+(8\pi^2\mu/h^2)[W+D_e-D_e\beta^2(1-y)^2/(\beta-y)^2]R=0.$$

Changing the independent variable to y, R is to be finite in $0 \leq y \leq \beta$. The indicial equation at $y=0$ is $\rho^2=-KW$, $K=8\pi^2\mu/h^2a^2$, and for real solutions finite at $y=0$, we must take $\rho=+\sqrt{(-KW)}$, $W<0$. Putting $R=y^\rho G$, and

changing the independent variable from y to z, $z=\beta-y$, the differential equation for G is

$$z^2(\beta-z)G''-z^2(2\rho+1)G'+A[(1+\beta)z-\beta(\beta-1)]G=0,$$

$$\beta\geq z\geq 0, \quad A=KD_e(\beta-1).$$

The indicial equation at $z=0$ is $\alpha(\alpha-1)=A(\beta-1)$. Taking the positive root and putting $G=z^\alpha F$, we solve the differential equation for F as a series in z.

$$z(\beta-z)F''+[2\alpha\beta-(2\rho+2\alpha+1)z]F'+[2A-(2\rho+1)\alpha]F=0.$$

Putting

$$F=\sum_{n=0}^{\infty} a_n z^n,$$

we obtain for the coefficients a_n the two-termed recurrence relation

$$a_{n+1}[(n+1)(\beta n+2\alpha\beta)]=a_n[n(n+2\rho+2\alpha)+(2\rho+1)\alpha-2A].$$

It will be seen that the series is not convergent at $z=\beta$, for $\beta a_{n+1}/a_n\sim 1+2\rho/n$ for large n, and therefore the series behaves like $(1-z/\beta)^{-2\rho}$. The solution R will thus be divergent at $z=\beta$, *i. e.*, at $r=\infty$, unless a restriction is imposed making the series for F terminate, for,

$$R=y^\rho z^\alpha F=\beta^\rho(1-z/\beta)^\rho z^\alpha F,$$

and unless F is a polynomial, F tends to infinity at $z=\beta$ more rapidly than $(1-z/\beta)^{-\rho}$. At $z=0$, *i. e.*, $r=0$, ψ is to be finite and therefore R/r must be finite. This is seen to be the case, for,

$$z^\alpha/r=(1-e^{-ar})^{\alpha-1}\beta^\alpha(1-e^{-ar})/r,$$

and this tends to zero at $r=0$ if $\alpha>1$. The condition that F is a polynomial of the nth degree in z is

$$2\rho=[B-n(n+2\alpha)]/(n+\alpha), \quad B=2A-\alpha, \quad n=0, 1, 2, \ldots.$$

But ρ is to be positive, and therefore $n(n+2\alpha)<B$, *i. e.*, $n<(B+a^2)^{\frac{1}{2}}-\alpha$. The vibrational states are thus given by

$$W=-\frac{1}{4K}\left[\frac{B-n(n+2\alpha)}{n+\alpha}\right]^2. \quad \ldots \quad (4)$$

It can be shown that this can be expanded in the form

of (2) for all $n \leq n(\text{max.})$, if $\beta > 5/3$. The expression (4) then becomes

$$W = -\frac{(2A-\frac{1}{4})^2}{K(4A(\beta-1)+1)} + \frac{(2A-\frac{1}{4})(2\beta A+\frac{1}{4})}{2K(A(\beta-1)+\frac{1}{4})^{3/2}}(n+\tfrac{1}{2}) - \frac{1}{4K}\left[\frac{3A^2(\beta+1)^2}{(A(\beta-1)+\frac{1}{4})^2}+1\right](n+\tfrac{1}{2})^2+ \ldots . \quad (5)$$

Calculation reveals that the parameter $a \sim 10^8$, and it will be seen that the coefficients in (5) are of the order of $10^{-12} : 10^{-14} : 10^{-16} : 10^{-26} \ldots$ Even when $n=n$ (max.), the orders of magnitude of the first few terms are $10^{-12} : 10^{-12} : 10^{-12} : 10^{-20} \ldots .$ From considerations of orders of magnitude it will be obvious that the first term differs very little from $-D_e$. Writing it as $D_e+\delta$, it can be shown that δ/D_e is of the order of 10^{-16}. On comparing the coefficients of $(n+\frac{1}{2})$ and $(n+\frac{1}{2})^2$ in (2) and (5) and eliminating β from the resulting equations, we obtain a quadratic equation for a in terms of μ, D_e, ω_e, and x_e. It can be shown that the lower root must be selected, and introducing approximations of the form

$$(D/K)^{\frac{1}{2}}(2\beta A+\tfrac{1}{4})/(A(\beta-1)+\tfrac{1}{4}) \sim (D/K)^{\frac{1}{2}}2\beta/(\beta-1),$$

we obtain

$$a = 9{\cdot}507 \times 10^{18}\omega_e(\mu/D_e)^{\frac{1}{2}}(\tfrac{3}{2}-Y),$$

$$\beta = 2/(2Y-1), \quad Y=(X-\tfrac{3}{4})^{\frac{1}{2}}, \quad X = 4x_e\omega_e D_e/\omega_e^2,$$

D_e being now expressed in cm.$^{-1}$. It will be seen that the solution in this form is valid for $1<X<3$.

The potential function is thus seen to give a relation of the form $r_e = r_e(\omega_e, x_e, D_e, \mu)$. It may be noticed that Morse's work provides an expression for D_e which we may write as $X=1$, and that our results depend upon the divergence from this law of the empirically determined quantities. A numerical study of data from band-spectra * reveals that while there is a considerable number of molecules for which $X>1$, there is also a large class for which $X<1$, and it is necessary to devise an approximation valid for this latter class. From the above comparison of coefficients, or by expanding the potential function about r_e and equating the coefficient

* W. Jevons, ' Report on Rand-spectra of Diatomic Molecules ' (1932): Appendix II.

of the first term $(r-r_e)^2$, to $2\pi^2\mu\omega_e^2$, we have approximately $2\beta(D_e/K)^{\frac{1}{2}}/(\beta-1)=ch\omega_e$. Taking this together with the result* $n(\text{max.})=\omega_e/2x_e\omega_e-\frac{1}{2}$, and introducing certain approximations of the form previously mentioned, we have

$$\beta=[2X-1+\sqrt{(1+4X-4X^2)}]/4(1-X)X,$$

$$a=3{\cdot}8\times10^{19}\sqrt{(D_e\mu)}\,.\,\omega_e x_e[1-\beta+\sqrt{(\beta^2-1)}]/\omega_e,$$

which is valid for $X<1$.

Calculation shows that, except for certain states of particular molecules, only approximate agreement with experiment obtains, but the analysis does indicate the existence of a relation of the type sought. The reasonable potential function does give reasonable results for the nuclear separation. It is to be presumed that a more accurate potential function will provide a more accurate expression for r_e.

§3. From the above analysis we have seen that the empirical result, that all except the first three terms in the expression (2) for W are extremely small, leads to the existence of a relation of the form $r_e=r_e(\omega_e, x_e, D_e, \mu)$. By way of illustration of the type of relation produced, we have carried out in detail the analysis for a particular form of the potential $U(r, r_e, D_e, a)$. But the general type of relation that has been predicted still involves one of the parameters, D_e, of the potential function, and further investigation is necessary before we can reproduce relations of the actual type that have been deduced from band-spectra data. The empirical relations are of the form $r_e=r_e(\omega_e)$, or $r_e=r_e(\omega_e, \mu)$, and are therefore of a less general type than has been predicted above. The conclusion is that, although band-spectra data do provide some knowledge of the form of the potential function, that knowledge is not sufficient to enable us to establish a relation of the required form between r_e and ω_e. It is therefore necessary to carry out an investigation into the general nature of the potential curves for diatomic molecules. To establish Morse's Law, it will be necessary to show in particular, that the expansion of the potential function in the neighbourhood of r_e has the form $U(r)=U(r_e)+(b\mu/r_e^6)(r-r_e)^2+$higher powers of $(r-r_e)$,

* W. Jevons, *loc. cit.* p. 194.

where b is a constant. The plausibility of the empirical relations from a theoretical point of view may be seen from the following general argument. The valency electrons of the two atoms may be considered to move in the field of central cores of effective charges Z and Z′ respectively, the effective charges depending on the shielding effect of the other electrons. This approximate treatment for atoms is well known. The potential energy, U, may be considered to consist of two parts, the electronic energy, E, and the potential energy, ZZ'/r, of the two cores. For large separations the electronic energy will be the sum of the separate energies of the valency electrons in the two unperturbed atoms, equal to $-R$, say. We now write for E, $E=-(R+c_1/r+c_2/r^2+\ldots)$, and suppose as a rough approximation that the coefficients may be so chosen that the resulting expression for U provides a tolerable approximation for all except very small nuclear separations. The condition that $U(r)$ has a minimum at r_e is $-ZZ'/r_e^2+c_1/r_e^2+2c_2/r_e^3+\ldots.=0$, that is, that the coefficient of $(r-r_e)$ in the expansion of $U(r)$ about r_e is zero. The expansion of $U(r)$ is then

$$U(r)=U(r_e)+[(ZZ'-c_1)/r_e^3-3c_2/r_e^4-6c_3/r_e^5-10c_4/r_e^6\ldots.](r-r_e)^2+\text{higher powers of } (r-r_e).$$

This may be written

$$U(r)=U(r_e)+k(r-r_e)^2+\ldots.,$$

where k is the bound force constant, and is equal to $2\pi^2\mu\omega_e^2$. We have for k,

$$(1/r_e^3)[(ZZ'-c_1)-3c_2/r_e6c_3/r_e^2-10c_4/r_e^3\ldots.].$$

But from Badger's modification of Morse's law

$$k=A(r_e-d_{ij})^{-3}=(A/r_e^3)[1+3d_{ij}/r_e+6d_{ij}^2/r_e^2+10d_{ij}^3/r_e^3\ldots.],$$

where A is a constant. Our approximate consideration of the problem has therefore produced a result comparable with Badger's law, and it appears that further investigation will provide a law in this form directly, rather than in the form given by Morse. In order to establish Badger's relation, it will, of course, be necessary to provide some theoretical evaluation of the constants, c_n, occurring in the expression for E. It will be expected that E will

depend on the effective nuclear charges, and therefore on the number of closed shells in each atom. E will, of course, also depend on the total number of valency electrons. The constants, c_n, will thus depend on the molecular periods of the two atoms and the molecular group number, and we shall expect a law of the type that has been suggested by Badger and by Clark. The theoretical determination of the general form of the electronic energy, E, for a diatomic molecule, and the actual relation, $r_e = r_e(\omega_e)$, that may be deduced, will appear in a subsequent paper. It is noted that results of interest may follow from an approximate analytical determination of the electronic energy analogous to the graphical method used by Condon * for the normal state of the hydrogen molecule, and to the equivalent method used by Gilbert † in the case of the higher energy levels of the hydrogen molecular ion, although more exact methods may be necessary in order to reproduce the actual empirical relations. The equivalent analytical method will consist in adjusting the constants, c_n, so that E is an expansion of a function having a finite value at $r=0$ equal to the electronic energy of the combined atom.

LX. *The Radioactivity of Potassium and Rubidium.* *By* F. H. Newman, *D.Sc., Professor of Physics, and* H. J. Walke, *M.Sc., Demonstrator in Physics, University College, Exeter* ‡.

1. *Introduction.*

POTASSIUM and rubidium show weak radioactivity. In both cases β-rays only are emitted, no α-rays having been observed, and no transmutation products have so far been detected. Biltz and Ziegert §, by partially separating the potassium isotopes, deduced that the heavier fraction contained the radioactive isotope, and it has been concluded therefore that the

* E. U. Condon, Proc. Nat. Acad. xiii. p. 466 (1927).
† C. Gilbert, Phil. Mag. ser. 7, xvi. p. 929 (1933).
‡ Communicated by Professor F. H. Newman.
§ *Phys. Zeits.* xxix. p. 197 (1925).

lighter isotopes, K_{19}^{39} and Rb_{37}^{85} are stable, the radioactivity being attributed to K_{19}^{41} and Rb_{37}^{87}, or other isotopes present in very small abundance.

The difference between the atomic weight of the normal potassium and that containing the radioactive isotope suggests that the activity of potassium is due to an isotope of mass 40, 41, or 42 ; so while it is apparent that the active isotope is of mass number higher than 39, uncertainty exists as to whether the isotope of mass 41, which has been observed by means of the mass spectrograph, is unstable, or whether the β-radioactivity has its origin in a missing isotope of mass number 40 or 42. Careful analysis of a special old specimen of biotite by Aston * revealed that the activity cannot be due to K_{19}^{41}, since he obtained no trace of a calcium line corresponding to mass number 41, whereas such an isotope—if it arose from the decay of K_{19}^{41}—should exist in such abundance that it would have been readily detected. Thus the radioactivity is due to K_{19}^{40} or K_{19}^{42}.

Gamow † suggested that the radioactivity of potassium and rubidium might arise from the β-ray activity of Cl_{17}^{36} and Br_{35}^{82} respectively, formed after the emission of α-particles from the missing isotopes K_{19}^{40} and Rb_{37}^{85}. This suggestion has recently been tested experimentally by Hevesy, Pahl, and Hosemann ‡, but no such α-particle emission was detected. These experimenters, however, found two β-ray components—in agreement with Bocciarelli §,—and assumed from this result that one and the same parent potassium atom emits two electrons. Such a transformation would lead to an isotope of scandium, and a search was made accordingly for a short-lived calcium isotope arising from the first of the two transformations. It was not detected, and they suggest from this negative result that the calcium isotope is of very short life, transmuting to a stable scandium isotope.

We suggest that the radioactivity of potassium consists of a single β-ray transformation, and that the strong components found by Hevesy, Pahl, and Hosemann

* ' Nature,' cxxxiii. p. 869 (1934).
† *Ibid.* cxxxiii. p. 744 (1934).
‡ *Ibid.* cxxxiv. p. 377 (1934).
§ Atti R. Acad. Lincei, xvii. p. 830 (1933).

are β-ray lines due to internal conversion of a nuclear γ-ray, resulting from the β-ray transformation, especially as disintegration electrons usually form a continuous spectrum, whereas components of fixed energy constitute the so-called line spectrum. In addition, the formation of a stable scandium isotope is improbable, since the heaviest potassium isotope which is likely to be radioactive has a mass number 42, and therefore the heaviest scandium which could result is Sc_{21}^{42}. But this isotope is radioactive *, emitting positive electrons according to the reaction

$$K_{19}^{39} + \alpha \rightarrow Sc_{21}^{42} + \overset{\nearrow}{n},$$

and

$$Sc_{21}^{42} \rightarrow Ca_{20}^{42} + \overset{+\nearrow}{e}.$$

Since Sc_{21}^{41} and Sc_{21}^{40}, if they exist, would certainly contain less protons than Sc_{21}^{42}, they would also certainly emit positrons, and therefore the formation of a scandium isotope from the radioactivity of potassium should result in positron radioactivity. This has not been observed experimentally, and we conclude therefore that the activity of potassium is due to K_{19}^{40} or K_{19}^{42}, the transmutation resulting in the emission of a single negative electron from each unstable nucleus.

2. *Missing, Unstable Isotopes.*

According to our theory † missing isotopes are radioactive, emitting β-rays, and on this theory both K_{19}^{40} and K_{19}^{42} could give rise to the activity of potassium. Similarly Rb_{37}^{86} and (or) Rb_{37}^{88} by transmutation would account for the activity of rubidium. We suggested that these unstable and missing isotopes could be produced by bombarding appropriate stable isotopes with neutrons—the formation corresponding to simple neutron capture, or disintegration with the emission of either α-particles or protons. Since there is apparently no potential barrier for neutrons, it appears that the neutron can penetrate nuclei at all energies, and simple neutron capture is most likely to occur if the energy of the bombarding neutrons is low.

* See Zwy, 'Nature,' cxxxiv. p. 64 (1934).
† Phil. Mag. xix. p. 661 (1935).

Hence we suggest that K_{19}^{40} and K_{19}^{42}, also Rb_{37}^{86} and Rb_{37}^{88}, can be formed by bombarding potassium and rubidium respectively with neutrons of low energy. If, as a result, there is an increase in the radioactivity of these elements this would confirm the suggestion that the activity arises from these isotopes, and, in addition, by separately testing the heavier and the lighter fractions of the partially separated potassium isotope it would be possible to detect the mass number of the radioactive isotope. The following reactions may occur when potassium is bombarded with neutrons :—

$$K_{19}^{39}+n\rightarrow K_{19}^{40}; \qquad K_{19}^{41}+n\rightarrow K_{19}^{42},$$

$$K_{19}^{39}+n\rightarrow Cl_{17}^{36}+\alpha; \qquad K_{19}^{41}+n\rightarrow Cl_{17}^{38}+\alpha,$$

$$K_{19}^{39}+n\rightarrow Ar_{18}^{39}+p; \qquad K_{19}^{41}+n\rightarrow Ar_{18}^{41}+p.$$

The unstable chlorine and argon isotopes, however, will probably have a short life, so that the only long-lived products would be the potassium isotopes.

The latter may also be produced from calcium according to the reactions

$$Ca_{20}^{40}+n\rightarrow K_{19}^{40}+p; \quad Ca_{20}^{42}+n\rightarrow K_{19}^{42}+p,$$

and so a long-life radioactivity (potassium) equal to that of potassium should result from bombarding calcium with neutrons of appropriate energy. The advantage of this method of preparation lies in the fact that the actual isotopes could be separated chemically from calcium. Moreover, since K_{19}^{39} and Ca_{20}^{40} are much more abundant than K_{19}^{41} and Ca_{20}^{42}, K_{19}^{40} would be the isotope most abundantly formed; so that any definite results from these two reactions would prove that K_{19}^{40} is responsible for the potassium activity.

A third method of producing K_{19}^{42} is by the bombardment of scandium with high-energy neutrons, viz.,

$$Sc_{21}^{45}+n\rightarrow K_{19}^{42}+\alpha,$$

and if as a result of this reaction β-ray activity—of life corresponding to that of potassium—is observed, then K_{19}^{42} is the radioactive isotope.

In connexion with the long-life radioactivity of potassium it is noteworthy that both argon and calcium have a stable isotope of mass number 40. Thus the configurations of 18 protons plus 22 neutrons and 20 protons plus 20 neutrons are both stable, whereas there is only one stable configuration of mass number 42 consisting of 20 protons and 22 neutrons. From this we infer that the long-life activity of potassium is due to K_{19}^{40}, since we can assume that both of the following changes are possible :—

$$K_{19}^{40} \rightarrow Ar_{18}^{40} + \overset{+}{e},$$

$$K_{19}^{40} \rightarrow Ca_{20}^{40} + \overset{-}{\beta},$$

each of which leads to a stable configuration.

3. *The Radioactivity of Rubidium.*

The existence of stable strontium isotopes of mass numbers 86, 87, and 88 suggests that the corresponding rubidium isotopes are unstable. As regards Rb_{37}^{87} there may be the following reactions :—

$$Kr_{36}^{87}\ (\text{unstable}) \rightarrow Rb_{37}^{87} + \overset{-}{\beta} \rightarrow Sr_{38}^{87} + \overset{-}{\beta}.$$

This could be tested experimentally by forming the parent krypton, viz.,

$$Kr_{36}^{86} + n \rightarrow Kr_{36}^{87},$$

or

$$Rb_{37}^{87} + n \rightarrow Kr_{36}^{87} + \overset{+}{p}.$$

The second of these reactions is the more promising, and if by bombarding rubidium with high-energy neutrons proton emission could be induced it should be possible to separate chemically the radioactive krypton. The latter may be tested for β-ray activity of a long-life period corresponding to that of the proposed unstable Rb_{37}^{87}.

Thus Rb_{37}^{86}, Rb_{37}^{87}, or Rb_{37}^{88} may all be the source of the rubidium activity. The first test to be made is by bombarding the element with low-energy neutrons. Any increase in the activity of long life after bombardment would indicate that the radioactivity was due to Rb_{37}^{86} or Rb_{37}^{88}, since these isotopes could be produced from Rb_{37}^{85} or Rb_{37}^{86} by simple neutron capture, whereas Rb_{37}^{87}

would not be so formed. With high-energy neutrons radioactive isotopes of other elements would be produced from rubidium, *e. g.*, Kr_{36}^{85} and Kr_{36}^{87} (corresponding to disintegration with proton emission) and Br_{35}^{82}, Br_{35}^{84} (corresponding to disintegration with α-particle emission). These isotopes are short-lived and would not interfere with the detection of the rubidium long-life activity.

Similarly, if strontium is bombarded with high-energy neutrons the following reactions may occur :

$$Sr_{38}^{86}+n\rightarrow Rb_{37}^{86}+\nearrow p,$$

$$Sr_{38}^{87}+n\rightarrow Rb_{37}^{87}+\nearrow p,$$

$$Sr_{38}^{88}+n\rightarrow Rb_{37}^{88}+\nearrow p,$$

and any radioactivity of long life resulting from this bombardment of strontium could arise from these three rubidium isotopes. In order to examine the possibility of Rb^{86} being radioactive we suggest that yttrium should be bombarded with high-speed neutrons and the result tested for β-radioactivity corresponding to the long-life activity of rubidium. If positive results are obtained the following reaction occurs :

$$Y_{39}^{89}+n\rightarrow Rb_{37}^{86}+\nearrow \alpha,$$

and Rb^{86} is the active isotope. Thus this experiment, combined with the others indicated above, will enable the actual radioactive isotope of rubidium to be identified.

In the yttrium reaction the following process may occur :

$$Y_{39}^{89}+n\rightarrow Sr_{38}^{89}+\nearrow p,$$

but the β-ray activity of the unstable Sr^{89} is likely to be of very short life compared with that of Rb^{86}.

In conclusion, therefore, any induced radioactivity of life corresponding to that of rubidium which arises when strontium is bombarded with high-speed neutrons indicates that Rb^{85} is stable and that Rb^{86}, Rb^{88} (both missing), or Rb^{87} is the source of the natural radioactivity of rubidium. Any increase in the intensity of this long-life activity, resulting from the bombardment of rubidium

with low-speed neutrons, proves that the isotopes of mass number 86 or 88 are radioactive; but if there is induced radioactivity of long life when yttrium is treated with high-speed neutrons then the activity is due to Rb^{86}. The fact that both Kr^{86}_{36} and Sr^{86}_{38} are stable suggests that Rb^{86}_{37} is the active rubidium isotope.

September 14, 1934.

LXI. *The Hall Effect and some other Physical Constants of Alloys.*—Part IV. *The Bismuth-Cadmium Series of Alloys. By* S. Gabe, *M.Sc., and* Prof. E. J. Evans, *D.Sc., Physics Department, University College, Swansea* *.

THIS investigation is a continuation of experiments † which have been carried out in the Physics Department of the University College of Swansea on the physical properties of binary alloy systems.

The curve connecting any physical property with composition is closely related to the equilibrium diagram of the alloy system under investigation. In some cases the curve is continuous, but in others it shows the existence of singular points corresponding either to a change of phase or to the presence of intermetallic compounds. The results of experiments on the physical properties of alloy systems should, therefore, give general confirmation of their equilibrium diagrams as deduced by metallurgists.

The equilibrium diagram ‡ of the bismuth-cadmium system is very simple, and consists of two branches meeting at the eutectic, which contains 40 per cent. by weight of cadmium and 60 per cent. by weight of bismuth. The temperature of crystallization at the composition corresponding to that of the eutectic is 140° C. According to this equilibrium diagram all the alloys are simply heterogeneous mixtures of bismuth and cadmium in various proportions.

* Communicated by the Authors.

† Part I.: "The Lead-Bismuth Series of Alloys," Phil. Mag. xvi. p. 329 (1933); Part II.: "The Tin-Bismuth Series of Alloys," Phil. Mag. xvii. p. 65 (1934).

‡ 'International Critical Tables,' ii. p. 426.

Stoffel *, from an investigation of the system, concluded that the metals—bismuth and cadmium—formed no solid solutions. Portevin †, who has also studied the system, concluded from a microscopic examination of the alloys that a solid solution of cadmium in bismuth may be present over the range of composition from 0 to 1 per cent. cadmium. According to Petrenko and Federow‡, who made a complete examination of the system, bismuth and cadmium form no solid solutions.

Herschkowitch § measured the potentials of bismuth-cadmium alloys against a normal solution of cadmium-sulphate, and found that their values were the same for alloys of all compositions. He therefore concluded that either the metals—bismuth and cadmium—form no solid solutions, or are soluble in one another to a very limited extent.

The magnetic susceptibility-composition curve of the system has been determined by Gnesotto and Binghinnotto ||, who were of the opinion that the steepness of the curve in the region of high bismuth content indicated the possibility of a slight solid solution of cadmium in bismuth. It is, therefore, seen that there is still some doubt as to the limited solubility of cadmium in bismuth.

In the present investigation the variation of the electrical resistivity, temperature coefficient of resistance, density, Hall effect, and specific heat of the bismuth-cadmium system of alloys with composition has been determined by measurements on the same specimens. As the values of the various constants of an alloy depend on its state, which is determined by casting temperature, rate of cooling, and other causes, the specimens used in the present investigation were carefully annealed. Consequently, the final measurements correspond to a definite reproducible state. The variations in physical properties with composition will later be compared with one another and discussed in relation to the equilibrium diagram.

Other researches dealing with the physical properties considered in this investigation have been carried out by Levin and Schottky ¶, who measured the specific

* *Zeit. Anorg. Chem.* liii. p. 148 (1907).
† *Rev. de Met.* iv. p. 389 (1907).
‡ *Zeit. für Metallkunde*, vi. p. 212 (1914).
§ *Zeit. Phys. Chem.* xxvii. p. 123 (1898).
|| *Real. Instit. Veneto Atti.* lxix. p. 1382 (1910).
¶ *Ferrum.* x. p. 192 (1913).

heats of the bismuth-cadmium alloys ; by Rudolfi *, and also by Broniewsky †, who measured the thermo-electric powers of the alloys.

Preparation and Analysis of the Alloys.

The bismuth-cadmium alloys employed in these experiments were prepared from comparatively pure materials. The cadmium was of 99·9 per cent. purity, and free from iron, arsenic, and antimony. The impurities in the bismuth were less than 0·1 per cent. by weight, the chief being :—Lead, ·06 per cent. ; silver, ·01 per cent. ; iron, ·01 per cent. The alloys were cast in the form of plates 14 cm. long, 2·5 cm. wide, and from 0·25 to 0·35 cm. thick. After preparation the plates were cleaned and planed down until their dimensions were uniform to within 0·5 per cent. Altogether, eighteen plates were cast ; two corresponding to the pure metals and the remaining sixteen to alloys of chosen compositions. The intended compositions were checked by chemical analysis.

In the method adopted a weighed quantity of the alloy was dissolved in nitric acid and the solution neutralized by the addition of ammonia. The bismuth was then precipitated as bismuth oxy-chloride by the addition of hydrochloric acid. The percentage of bismuth in the alloy could then be calculated and the percentage of cadmium obtained by difference.

Annealing.

The alloys were placed inside an electric furnace, which was then evacuated to a low pressure and the heating current adjusted so that the temperature of the furnace reached 125° C. After the alloys had been kept at this temperature for days the furnace was allowed to cool gradually to room-temperature. The alloys were then removed from the furnace and their resistivities measured at 0° C. The annealing was repeated over long periods until the resistivities of the alloys assumed constant values. The alloys were then considered to have reached their final reproducible states and were used for the determinations of the various physical constants.

* *Zeit. Anorg. Chem.* lxvii. pp. 65–96 (1910).
† *Rev. de Met.* vii. p. 341 (1910).

Measurements of Physical Constants.

As the methods employed in the determination of the Hall coefficients and other physical constants of the alloys have been already described in detail in a previous paper *, it is only necessary to make a brief reference to a few points connected with measurements.

Resistivity.

The resistivities of the alloys were measured at 0° C. immediately after preparation, and also in the annealed state. The experimental results are collected in Table I.

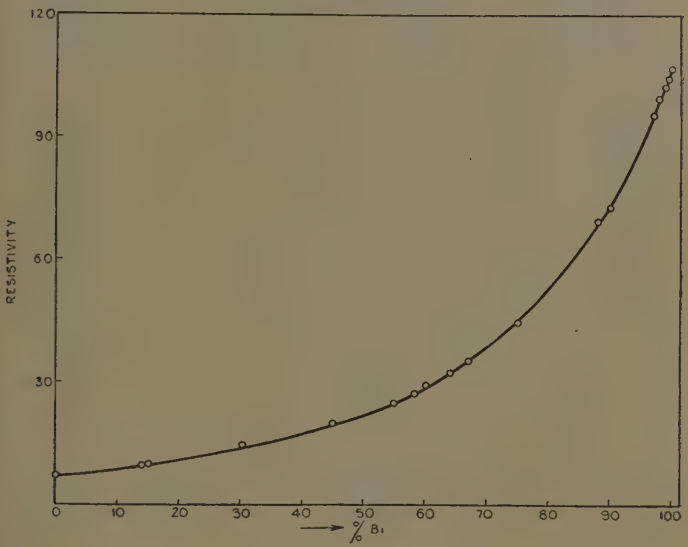
TABLE I.

Composition by weight.	Resistivity at 0° C. in microhms per cm.	
	Before annealing.	After annealing.
100·0 per cent. Cd	7·07	6·83
14·1 „ „ Bi.....	..	9·67
14·9 „ „ Bi.....	12·56	10·03
30·4 „ „ Bi.....	16·67	14·67
45·0 „ „ Bi.....	20·13	20·16
55·0 „ „ Bi.....	25·57	25·11
58·3 „ „ Bi.....	28·93	27·50
60·0 „ „ Bi.....	30·78	29·23
64·0 „ „ Bi.....	33·90	32·49
67·0 „ „ Bi.....	36·19	35·32
75·0 „ „ Bi.....	48·38	44·90
88·0 „ „ Bi.....	..	69·41
90·0 „ „ Bi.....	71·04	73·01
97·1 „ „ Bi.....	95·88	95·57
98·0 „ „ Bi.....	100·10	99·40
99·0 „ „ Bi.....	103·80	102·20
99·5 „ „ Bi.....	106·40	104·50
100·0 „ „ Bi.....	107·40	106·80

* Part I.: "The Lead-Bismuth Series of Alloys," *loc. cit.*

and plotted in Graph I. It is estimated that on the average the experimental errors are not greater than 0·4 per cent.

Graph I.



Mean Temperature Coefficient of Resistance.

The mean temperature coefficient of resistance of the various alloys were measured over the range 0° to 100° C. The experimental results for the annealed alloys are given in Table II. and plotted in Graph II. The errors in the determinations are estimated to be not greater than 0·5 per cent. on the average.

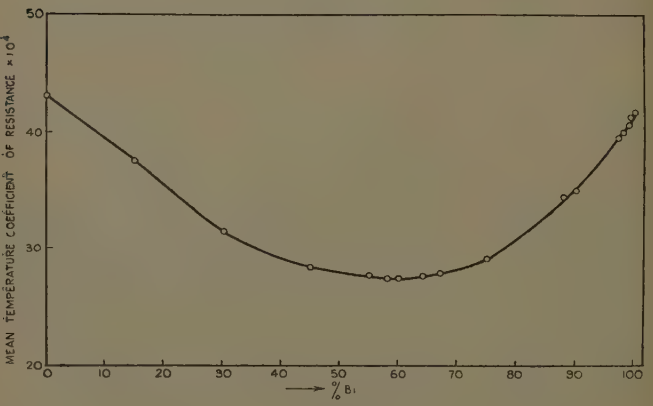
Thermoelectric Power.

The mean thermoelectric powers of the alloys with respect to pure electrolytic copper have been determined over the temperature range 12°–100° C. It is estimated that the errors in the results are not greater than 0·3 per cent. on the average. The experimental results are collected in Table III. and plotted in Graph III.

TABLE II.

Composition by weight.	Mean temp. coeff. of resistance between 0° and 100° C. $\times 10^4$.	Composition by weight.	Mean temp. coeff. of resistance between 0° and 100° C. $\times 10^4$.
100·0 per cent. Cd ..	43·00	67·0 per cent. Bi ..	27·90
14·1 „ „ Bi ..	38·70	75·0 „ „ Bi ..	29·32
14·9 „ „ Bi ..	37·53	88·0 „ „ Bi ..	34·70
30·4 „ „ Bi ..	31·50	90·0 „ „ Bi ..	35·10
45·0 „ „ Bi ..	28·47	97·1 „ „ Bi ..	39·61
55·0 „ „ Bi ..	27·81	98·0 „ „ Bi ..	40·09
58·3 „ „ Bi ..	27·58	99·0 „ „ Bi ..	40·69
60·0 „ „ Bi ..	27·54	99·5 „ „ Bi ..	41·43
64·0 „ „ Bi ..	27·74	100·0 „ „ Bi ..	41·73

Graph II.



Density.

The results are collected in Table IV. and plotted in Graph IV. It is estimated that the experimental errors in the determinations of the densities are not greater than 0·13 per cent.

TABLE III.

Composition by weight.	Thermoelectric power with respect to copper in microvolts per ° C.	Composition by weight.	Thermoelectric power with respect to copper in microvolts per ° C.
100·0 per cent. Cd ..	+ 1·701	75·0 per cent. Bi ..	−31·44
14·9 „ „ Bi ..	− 0·798	88·0 „ „ Bi ..	−44·42
30·4 „ „ Bi ..	− 5·872	90·0 „ „ Bi ..	−47·43
45·0 „ „ Bi ..	−11·85	97·1 „ „ Bi ..	−59·76
55·0 „ „ Bi ..	−16·98	98·0 „ „ Bi ..	−61·40
58·3 „ „ Bi ..	−18·91	99·0 „ „ Bi ..	−62·76
60·0 „ „ Bi ..	−19·93	99·5 „ „ Bi ..	−63·81
64·0 „ „ Bi ..	−22·49	100·0 „ „ Bi ..	−64·40
67·0 „ „ Bi ..	−25·01		

Graph III.

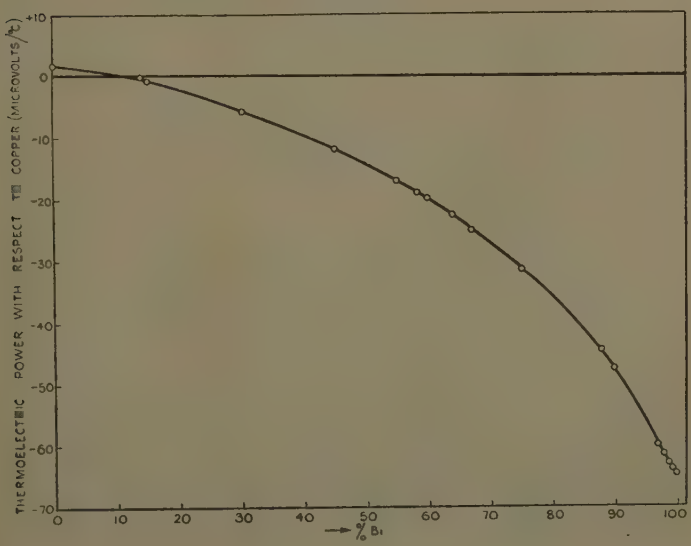
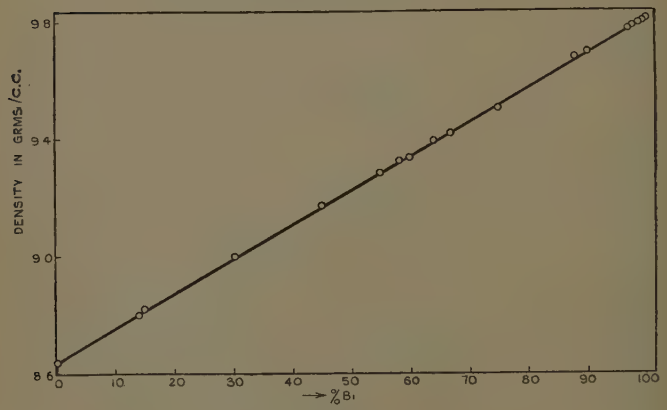


TABLE IV.

Composition by weight.	Density in grm. per c.c. at 16° C.	Composition by weight.	Density in grm. per c.c. at 16° C.
100·0 per cent. Cd. ..	8·64	67·0 per cent. Bi ..	9·41
14·1 „ „ Bi ..	$8{\cdot}80_4$	75·0 „ „ Bi ..	9·50
14·9 „ „ Bi ..	8·82	88·0 „ „ Bi ..	$9{\cdot}67_4$
30·4 „ „ Bi ..	9·00	90·0 „ „ Bi ..	9·69
45·0 „ „ Bi ..	9·17	97·1 „ „ Bi ..	9·77
55·0 „ „ Bi ..	9·28	98·0 „ „ Bi ..	9·78
58·3 „ „ Bi ..	9·32	99·0 „ „ Bi ..	9·79
60·0 „ „ Bi ..	9·33	99·5 „ „ Bi ..	9·79
64·0 „ „ Bi ..	9·39	100·0 „ „ Bi ..	9·80

Graph IV.



Hall Effect.

The Hall coefficient of pure bismuth has a large negative value, and that of pure cadmium a comparatively small positive value. All the alloys examined in this investigation have negative Hall coefficients, but their magnitudes are much greater for alloys at the bismuth end of the series than for those at the cadmium end. The Hall

Table V.

Composition by weight.	Temp. in ° C.	Hall coefficients $\times 10^2$. Magnetic fields in gauss. 3096.	4630.	5787.	6795.	7661.	8424.
100·0 per cent. Cd ..	19·8	+ 0·0530	+ 0·0532	+ 0·0529	+ 0·0532	+ 0·0529	+ 0·0532
14·9 „ „ Bi	19·0	− 0·199	− 0·161	− 0·136	− 0·117	− 0·106	− 0·0995
30·4 „ „ Bi	19·1	− 1·40	− 1·17	− 0·997	− 0·850	− 0·744	− 0·673
45·0 „ „ Bi	19·6	− 6·02	− 4·97	− 4·36	− 3·89	− 3·22	− 3·04
55·0 „ „ Bi	20·3	− 11·67	− 9·79	− 8·63	− 7·69	− 6·90	− 6·44
58·3 „ „ Bi	21·0	− 15·3	− 13·0	− 11·5	− 10·4	− 9·34	− 8·68
60·0 „ „ Bi	15·4	− 19·5	− 16·2	− 14·1	− 12·7	− 11·4	− 10·6
64·0 „ „ Bi	16·0	− 29·7	− 24·3	− 20·8	− 18·1	− 16·3	− 15·2
67·0 „ „ Bi	22·5	− 38·5	− 32·4	− 28·0	− 24·9	− 22·8	− 21·4
75·0 „ „ Bi	19·4	− 69·1	− 60·0	− 55·3	− 47·7	− 43·3	− 40·4
90·0 „ „ Bi	19·0	−197·0	−171·9	−153·0	−137·0	−127·0	−122·0
97·1 „ „ Bi	18·4	−372	−334	−316	−300	−292	−285
98·0 „ „ Bi	18·9	−428	−388	−363	−342	−333	−325
99·0 „ „ Bi	15·5	−510	−456	−419	−396	−384	−378
99·5 „ „ Bi	15·5	−608	−548	−512	−483	−469	−464
100·0 „ „ Bi	19·1	−721	−654	−610	−582	−569	−561

coefficient of an alloy of given composition also depends upon the intensity of the magnetic field, the negative coefficient decreasing in magnitude as the intensity of the field increases. The accuracy of the experimental results will, therefore, depend on both the composition of the alloy and on the intensity of the magnetic field.

Graph V.

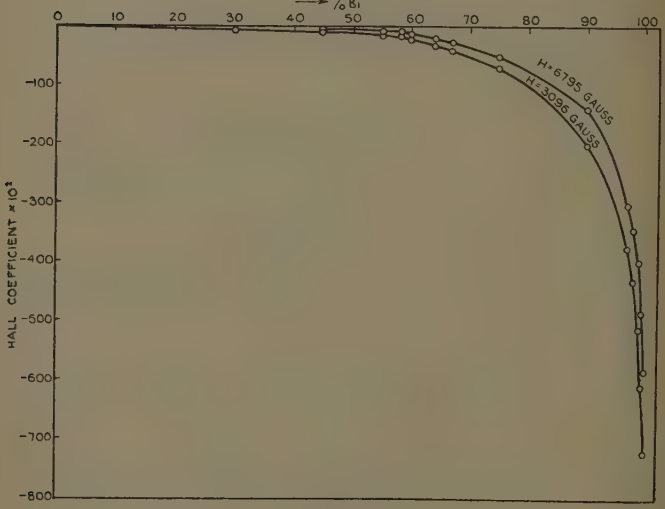


TABLE VI.

Composition by weight.	Mean specific heat between 19° C. and 100° C.	Composition by weight.	Mean specific heat between 19° C. and 100° C.
100·0 per cent. Cd ..	·0559	67·0 per cent. Bi ..	·0386
14·9 „ „ Bi ..	·0520	75·0 „ „ Bi ..	·0365
30·4 „ „ Bi ..	·0482	90·0 „ „ Bi ..	·0327
45·0 „ „ Bi ..	·0443	97·1 „ „ Bi ..	·0308
55·0 „ „ Bi ..	·0418	98·0 „ „ Bi ..	·0305
58·3 „ „ Bi ..	·0409	99·0 „ „ Bi ..	·0303
60·0 „ „ Bi ..	·0406	99·5 „ „ Bi ..	·0302
64·0 „ „ Bi ..	·0394	100·0 „ „ Bi ..	·0301

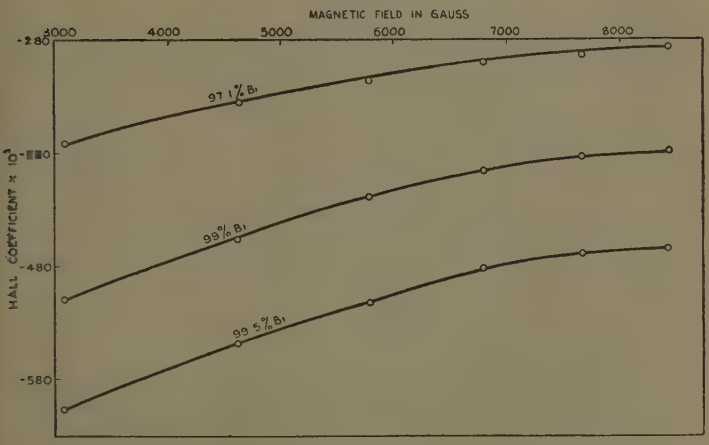
For alloys of high bismuth content it is estimated that the experimental errors are less than 0·6 per cent. ; but for alloys of high calcium content the errors are greater and in the neighbourhood of 1 per cent. The errors in the determinations of magnetic fields are less than 1 in 200.

The experimental results are recorded in Table V. and plotted in Graphs V. and VI.

Specific Heat.

The specific heats of the alloys were determined by means of a Joly steam calorimeter in the usual manner.

Graph VI.



The mean specific heats between 19·5° and 100° C. are collected in Table IV. and plotted in Graph VII. It is estimated that the results are accurate to within 1 per cent. on the average.

Discussion of Results.

The physical properties examined in this investigation are of two kinds, one kind involving the passage of an electric current through the alloys and the other not. The experimental results show that the density-composition and the specific heat-composition curves are linear.

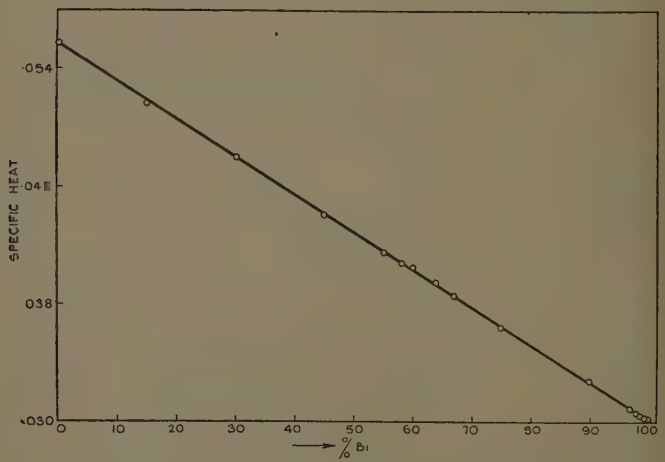
A similar result for the variation of specific heat with composition was previously obtained by Levin and Schottky *.

From the values contained in Tables IV. and VI. it can be calculated that the density (d) and the mean specific heat (s) of an alloy containing X per cent. by weight of bismuth are given by the following equations :—

$$d = 8{\cdot}64 + 1{\cdot}16 \times 10^{-2}\mathrm{X},$$

$$s = {\cdot}0559 - 2{\cdot}58 \times 10^{-4}\mathrm{X}.$$

Graph VII.



The experimental results relating to the densities and specific heats of the alloys therefore support the conclusion that there is no solid solution of bismuth in cadmium or of cadmium in bismuth. The alloys are simply mixtures of bismuth and cadmium crystals in various proportions. The evidence is, however, not conclusive, as the presence of slight solid solutions would probably not materially alter the above results for density and specific heat.

The variations of the resistivity, temperature coefficient of resistance, thermoelectric power, and Hall coefficient

* Levin and Schottky, *loc. cit.*

with composition by weight of the alloy are represented, within experimental error, by smooth curves. These curves lie either above or below the straight line joining the values of the particular physical property for pure cadmium and pure bismuth, and give no indication of well-defined singular points showing the existence of intermetallic compounds or the end of a solid solution phase. On the other hand, Rudolfi *, from an examination of the thermoelectric power-composition curve, found evidence of a slight change of slope at the composition corresponding to 90 per cent. of bismuth, but was unable to account for it. He was, however, of the opinion that there existed solid solutions of cadmium in bismuth having a small concentration.

An examination of the curves dealing with the electrical properties, with the exception of the temperature coefficient of resistance curve, shows that the variation of the physical properties with composition is far more rapid at the bismuth end of the series than at the cadmium end. There is, however, no certain evidence of a discontinuity in the curves in the region between 97 per cent. and 100 per cent. bismuth.

The resistivity (ρ) and the thermoelectric power (P) of an alloy containing X per cent. by weight of bismuth can be represented by the equations :—

$$\rho = 6{\cdot}83 + {\cdot}168X + {\cdot}00270X^2 + 56{\cdot}2 \times 10^{-12}X^6$$

$$P = 1{\cdot}701 - {\cdot}130X - {\cdot}00380X^2 - 15{\cdot}1 \times 10^{-14}X^7.$$

The differences between the values calculated from the above equations and the experimental values are not greater than about 1 per cent. on the average.

The effect of annealing on the resistivities of the alloys is shown in Table I. With one or two exceptions the resistivities diminish on annealing, the change being greatest for the alloy containing 14·9 per cent. by weight of bismuth.

In the bismuth-tin and bismuth-lead series of alloys † reversals of the sign of the Hall coefficient occur for some compositions as the intensity of the magnetic field is varied from 3096 to 8424 gauss. The bismuth-cadmium system of alloys exhibits no such reversals over the same

* Rudolfi, *loc. cit.*

† *Loc. cit.*

range of the magnetic field, and the Hall coefficient-magnetic field curves (Graph VI.) flatten out as the intensity of the magnetic field is increased. These results suggest that no reversal is likely even at much higher fields than those employed in the present investigation. It is interesting to note that the metals tin and lead, which produce these reversals, have similar chemical properties and belong to group IV. of the Periodic Table, whilst cadmium is a member of group II. of the same Table.

The relation between the Hall coefficient and the composition of the bismuth-cadmium alloys for magnetic fields of 3096 and 6795 gauss is shown in Graph V. Similar curves are obtained by plotting the Hall coefficients for the other fields. The Hall coefficient of pure cadmium has a small positive value, and that of pure bismuth a large negative value. The Hall coefficients of all the alloys examined in this investigation are negative for each magnetic field, and Graph V. indicates that the negative value of the coefficient for a constant field increases as the percentage of bismuth in the alloy increases. The curves are very steep at the bismuth end of the series.

The negative value of the Hall coefficient of each alloy diminishes as the strength of the magnetic field is increased. This result, which is clearly indicated in Graph VI., is also true of pure bismuth, as shown in Table V.

Comparing the electrical resistivity-composition and the Hall coefficient-composition curves, it is seen that a high negative value of the Hall coefficient corresponds to a high resistivity. This result may possibly be expected on simple electron theories of electrical conduction and of the Hall coefficient. According to these theories, both the resistivity and the Hall coefficient vary inversely as the number of electrons per unit volume. If it is assumed that the addition of cadmium to bismuth does not produce much variation in the mean free path of the electrons, and also that the temperature is constant, it follows that a diminution in the negative value of the Hall coefficient of pure bismuth by the addition of cadmium should be accompanied by a corresponding diminution in the resistivity, as is shown by the experimental results.

Although all the alloys employed in the present investigation have a negative Hall coefficient, it is evident from the negative value of the coefficient for bismuth

and the positive value for cadmium that the Hall coefficient-composition curve must cross the axis of zero Hall coefficient at a composition of high cadmium content. It is difficult to give a satisfactory explanation of these results.

The general trend of the thermoelectric power-composition curve as the percentage of bismuth is increased is also similar to that of the Hall coefficient-composition curve; but the latter is far steeper at the bismuth end of the system.

As previously pointed out, the curves showing the relation between the physical properties of the alloys and their composition do not show definite singular points corresponding to phase boundaries and therefore support the conclusions that the system consists of a mixture of bismuth and cadmium crystals in varying proportions.

The resistivity, thermoelectric power, and especially the Hall coefficient curves show rapid variations at the bismuth end of the series and indicate that the presence of small quantities of cadmium has a considerable effect on these physical properties. However, if there is a solid solution of small concentration at the bismuth end of the series, it has not been found possible in the present investigation to fix its limits.

LXII. *On the Radiation Resistance of Parallel Wire High-Frequency Transmission Lines.* *By* S. S. Banerjee, *M.Sc., Demonstrator in Physics, Hindu University, Benares* *.

Introduction.

In recent years much attention has been directed towards radio communication with micro-waves of length 5 metres and below. Such waves possess several advantages. The aerial system is of small dimensions and the transmission is free from atmospherics and fading, and as such they are used for radio beacons for communication over short distances and also for city broadcasting. The aerial system being necessarily

* Communicated by Prof. S. K. Mitra, D.Sc.

located remote from obstructions by buildings, trees, etc., the energy to it has to be fed by means of transmission lines from the high-frequency generator situated on the ground. The transmission line has to be carefully designed and laid out in order that it may not be a source of spurious radiation. Two types of transmission lines are generally used—one the parallel wire system, consisting of a pair of parallel wires, and the other concentric cables. Whichever system is used there are always likely to be several curves and bends along the run of the transmission line from the generator to the aerial system. The presence of such bends considerably modify the constants of the line and offer sources of radiation. A critical study of the change of the line constants due to the presence of bends is therefore useful from the practical point of view. In the present communication is described the results of study, both theoretical and experimental, of the change in the radiation resistance of the first type of the transmission lines, namely, the parallel wire system, when it is bent along its length. Two types of bends have been studied; first, when the pair of wires is bent in its own plane, and second, when it is bent such that the perpendicular to the plane containing the bent arms is parallel to the shortest length between the wires. It has been found that for the first case considerable change in the radiation resistance is produced when the angle between the bent arms is small. For case two, on the other hand, the radiation resistance is hardly if at all changed even when the angle between the bent portions is small. As a preliminary study the variation in the radiation resistance of a simple straight parallel wire system for various separations between the two wires has been investigated.

List of Symbols used.

α, attenuation constant.
A, a constant.
β, wave-length constant.
B, a constant and function of R and P.
C, capacity of the parallel wires per unit length.
Ci (x), cosine integral of x.
δ, deflexion in the indicating instrument.
D, a constant and function of L and M.
ϵ, 0·5772, Euler's constant.

E_x, component of electric intensity perpendicular to the wire.
E_y, component of electric intensity parallel to the wire.
F, a constant and function of C and N.
G, leakance of the parallel wires per unit length.
θ, angle between the bent arms.
I_0, instantaneous current in ampere in the wire.
I, R.M.S. current in ampere in the wire.
K, shortest distance between the parallel wires.
l, length of the wire from the input end.
L, inductance of the parallel wires per unit length.
μ, permeability.
m, $2\pi/\lambda$.
M, inductance at the input end of the wires.
N, capacity at the input end of the wires.
P, resistance at the input end of the wires.
ρ, resistivity.
R, resistance of the parallel wires per unit length.
Si (x), sine integral of x.
σ, diameter of the wires.
x, distance in the direction perpendicular to the wire.
y, distance in the direction parallel to the wire.
v, velocity of light.

Theoretical Considerations.

Case 1. *Radiation Resistance of Straight Parallel Wires.*

There are two methods available for this purpose. In the first, called the "Poynting vector" method, we calculate the Poynting vector for each point of space and integrate the normal energy flow through any surface enclosing the wire. This method suffers from the defect that we cannot obtain the contributions to the radiated power from different points of the wire. The second method, known as the method of "induced E.M.F."[1, 2, 3, 4], is based on the electromagnetic field equations after Lorentz. This method is used in the present investigation, and its outline is given below.

AB is a conductor (fig. 1) in which flows a high frequency current of known frequency and known distribution. The electric field at any point 0 due to the current can be found from a consideration of the scalar and the vector potentials at the point in question. If the distribution of the current along the wire follows a sine law—

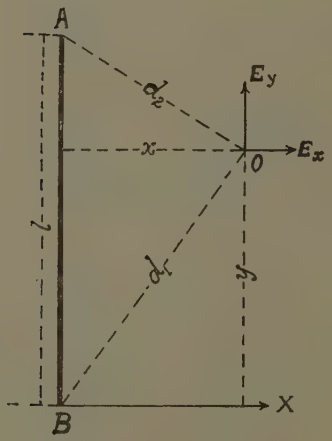
that is, current at any point $x=I_0 \sin mx$—then it may be shown after Carter [3] that, if l is some integral multiple (n) of half wave-length,

$$E_x = -j30I\left[\frac{e^{-jmd_2}}{d_2} \cdot \frac{y}{x} - \frac{l}{x}(-1)^n - \frac{e^{-jmd_1}}{d_1} \cdot \frac{y}{x}\right] \text{volts per cm.,} \quad . \quad . \quad . \quad (1)$$

and

$$E_y = j30I\left[\frac{e^{-jmd_2}}{d_2}(-1)^n - \frac{e^{-jmd_1}}{d_1}\right] \text{volts per cm.,} \quad . \quad (2)$$

Fig. 1.



where d_1 and d_2 are the distances from the ends of the wire.

In order to find out the radiation resistance of a wire we have to find out the value of the electric field in the wire itself. From the value of E_y the radiation resistance for the whole wire can be readily calculated and written as

$$R_{11} = 30[\epsilon + \log(2ml) - \text{Ci}(2ml)] \text{ ohms.} \quad . \quad . \quad (3)$$

In the case of parallel wires the total value of E_y at any point in one of the wires is due to the resultant of the intensity due to that particular wire itself and

to that due to the other wire. If the simplifying assumptions that the wires are multiples of half wave-lengths and not displaced in height are made, the value of the radiation resistance of one wire due to the other wire is given by

$$R_{12}=30[2\mathrm{Ci}(mk)-\mathrm{Ci}\, m(\sqrt{k^2+l^2}+l)-\mathrm{Ci}\, m(\sqrt{k^2+l^2}-l)]$$

ohms. . . . (4)

If the currents in the two wires are in antiphase the total radiation resistance is given by

$$R_T=2(R_{11}-R_{12})$$
$$=60[\epsilon+\log_e(2ml)-\mathrm{Ci}\,(2ml)-2\mathrm{Ci}\,(mk)$$
$$+\mathrm{Ci}\, m(\sqrt{k^2+l^2}+l)+\mathrm{Ci}\, m(\sqrt{k^2+l^2}-l)] \text{ ohms.}$$

We have used this formula for calculating the radiation resistance of a pair of parallel wires of length $\lambda/2$ for various separations ranging from $\lambda/60$ to $\lambda/10$. The calculation as well as experimental observations show that the radiation becomes appreciable only when the separation becomes greater than $\lambda/20$. The details of the theory of the experiment and observed results are given in the following sections.

Case 2. *Radiation Resistance of Parallel Wires bent in their own Plane.*

In order to find out the radiation resistance of the whole system we shall have first to consider separately the contribution to the electric intensity at any point along any one of the arms by all the four arms.

Let the point under consideration be situated at any point 0 in wire 3 (fig. 2). The contribution to the electric intensity at this point from wire 3 itself may be found after the manner indicated in the preceding case. The contribution from wire 4, which is parallel to 3 but displaced in height, may be found after Carter [3]. The contribution of wire 2, which meets 3 at an angle, may also be found after Carter. The contribution from wire 1, which is inclined to 3 but unlike 2 does not meet 3, is calculated below.

From fig. 2 it will be clear that

$$x = k + r \sin\theta$$

and

$$y = k \cot\theta/2 + r\cos\theta,$$

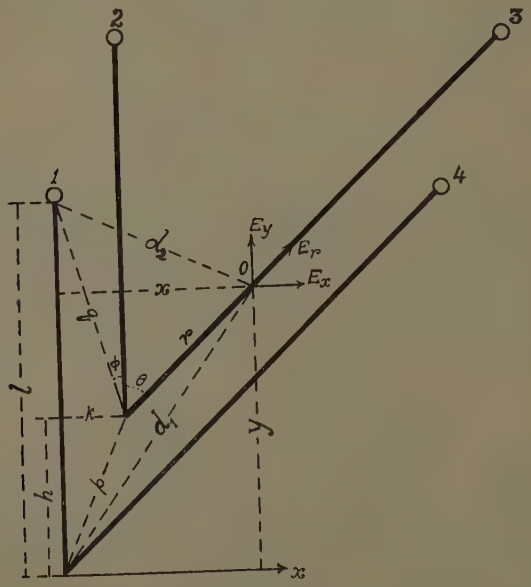
and d_1 may be written as

$$\sqrt{p^2 + r^2 + 2pr\cos\theta/2}$$

and d_2 as

$$\sqrt{q^2 + r^2 - 2qr\cos(\theta+\phi)}.$$

Fig. 2.



Substituting these values of x, y, d_1, and d_2 in equations (1) and (2), we get

$$\mathrm{E}_x = -j30\mathrm{I}\Big[\frac{e^{-jm\sqrt{q^2+r^2-2qr\cos(\theta+\phi)}}}{\sqrt{q^2+r^2-2qr\cos(\theta+\phi)}}(-1)^n \cdot \frac{k\cot\theta/2 + r\cos\theta - l}{k + r\sin\theta},$$

$$- \frac{e^{-jm\sqrt{p^2+r^2+2pr\cos\theta/2}}}{\sqrt{p^2+r^2+2pr\cos\theta/2}} \cdot \frac{k\cot\theta/2 + r\cos\theta}{k + r\sin\theta}\Big],$$

and

$$E_y = j30I\left[\frac{e^{-jm\sqrt{q^2+r^2-2qr\cos(\theta+\phi)}}}{\sqrt{q^2+r^2-2qr\cos(\theta+\phi)}}(-1)^n - \frac{e^{-jm\sqrt{p^2+r^2+2pr\cos\theta/2}}}{\sqrt{p^2+r^2+2pr\cos\theta/2}}\right].$$

Since $E_r = E_x \sin\theta + E_y \cos\theta,$

where E_y is the electric intensity along the wire 3, the value of R_{31} can be written as

$$30\cos\theta\left[\int_0^l \frac{\sin m\sqrt{q^2+r^2-2qr\cos(\theta+\phi)}}{\sqrt{q^2+r^2-2qr\cos(\theta+\phi)}}\cdot\sin mr\,dr + \frac{\sin m\sqrt{p^2+r^2+2pr\cos\theta/2}}{\sqrt{p^2+r^2+2pr\cos\theta/2}}\cdot\sin mr\,dr\right]$$

$$-30\sin\theta\left[\int_0^l \frac{\sin m\sqrt{q^2+r^2-2qr\cos(\theta+\phi)}}{\sqrt{q^2+r^2-2qr\cos(\theta+\phi)}}\left(\frac{k\cot\theta/2+r\cos\theta-l}{k+r\sin\theta}\right)\sin mr\,dr + \int_0^l \frac{\sin m\sqrt{p^2+r^2+2pr\cos\theta/2}}{\sqrt{p^2+r^2+2pr\cos\theta/2}}\left(\frac{k\cot\theta/2+r\cos\theta}{k+r\sin\theta}\right)\sin mr\,dr. \quad . \quad . \quad . \quad (5)$$

Due to the contribution to the electric intensity from wire 4 on 3, the radiation resistance for them is given by Carter as

$$R_{34} = -15\cos mh\,[-2\mathrm{Ci}\,m(\sqrt{k^2+h^2}+h) - 2\mathrm{Ci}\,m(\sqrt{k^2+h^2}-h) + \mathrm{Ci}\,m\{\sqrt{k^2+(h-l)^2}+(h-l)\} + \mathrm{Ci}\,m\{\sqrt{k^2+(h-l)^2}-(h-l)\} + \mathrm{Ci}\,m\{\sqrt{k^2+(h+l)^2}+(h+l)\} + \mathrm{Ci}\,m\{\sqrt{k^2+(h+l)^2}-(h+l)\}] + 15\sin mh\,[2\,\mathrm{Si}\,m(\sqrt{k^2+h^2}+h) - 2\,\mathrm{Si}\,m(\sqrt{k^2+h^2}-h) - \mathrm{Si}\,m\{\sqrt{k^2+(h-l)^2}+(h-l)\} + \mathrm{Si}\,m\{\sqrt{k^2+(h-l)^2}-(h-l)\} - \mathrm{Si}\,m\{\sqrt{k^2+(h+l)^2}+(h+l)\} + \mathrm{Si}\,m\{\sqrt{k^2+(h+l)^2}-(h+l)\}], \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (6)$$

where $$h=k\cot\theta/2.$$

Resistance for wires 3 and 2 is given by

$$R_{32}=30l\int_0^l \frac{\sin md}{d}\cdot\frac{\sin mr}{r}\,dr, \quad . \quad . \quad . \quad (7)$$

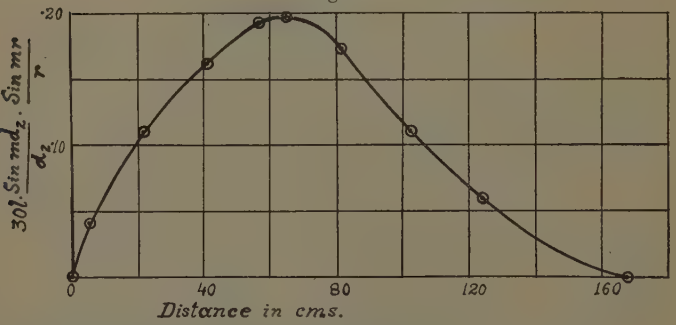
where d is the distance from the end of wire 2 to the point 0 on wire 3, and is equal to

$$\sqrt{l^2+r^2-2lr\cos\theta},$$

not shown in the diagram.

As there are four arms of the system the total resistance will be four times the resistance calculated for one arm.

Fig. 3.



Taking account of the phases of the current in the various arms we may write the total resistance

$$R_T=4(R_{33}-R_{34}+R_{31}-R_{32}).$$

Of these R_{33} and R_{34} can be calculated from the equations (3) and (6). R_{31} and R_{32} are computed graphically from integrals given in equations (5) and (7), as their forms are not convenient for integration. A specimen of the graphs from which numerical values are calculated is shown in fig. 3.

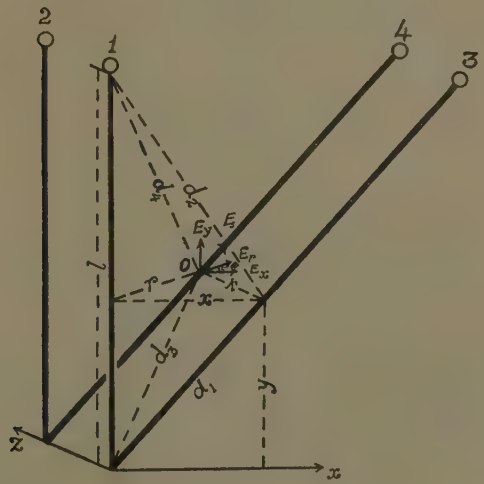
Case 3. *Radiation Resistance of Parallel Wires bent such that the perpendicular to the plane containing the bent arms is parallel to the shortest length between the Wires.*

This case is more complicated, as all the wires are not in the same plane. Suppose the point 0 under considera-

tion is situated on wire 4 (fig. 4). The contribution to the electric intensity at this point by wires 2 and 3 can be found as usual, and the contribution from wire 1, which is inclined to 4, but unlike 2 does not meet 4 and is displaced along the z-axis, is calculated below.

Here, since E_r is in a plane containing the wire 1 and the lines d_3 and d_4, E_r, the component of E_r in the direction of the x-axis, is $E \cos \phi$, where ϕ is the angle between this plane and the plane of the paper. If E_s

Fig. 4.



be the total intensity due to E_x and E_y along the wire 4, and if s be the distance along the wire,

$$E_s = E_x \sin\theta + E_y \cos\theta$$

$$= E_r \cos\phi \sin\theta + E_y \cos\theta$$

$$= j30I \frac{e^{-jmd_4}}{d_4} (-1)^n \cos\theta + j30I \frac{e^{-jmd_3}}{d_3} \cos\theta$$

$$-(-1)^n j30I \frac{e^{-jmd_4}}{d_1} \cos\theta \cos\phi + j30I \frac{l}{s} \frac{e^{imd_4}}{d_4} (-1)^n \cos\phi$$

$$+ j30I \frac{e^{-jmd_3}}{d_3} \cos\theta \cos\phi.$$

From this we get

$$R_{41}=30\cos\theta\int_0^l \frac{\sin md_4}{d_4}\sin ms\,ds$$
$$+30\cos\theta\int_0^l \frac{\sin md_3}{d_3}\sin ms\,ds$$
$$-30\cos\theta\int_0^l \frac{\sin md_4}{d_4}\sin ms\cos\phi\,ds$$
$$+30l\int \frac{\sin md_3}{d_3}\sin ms\cos\phi\,ds$$
$$+30l\int_0^l \frac{\sin md_4}{d_4}\sin\frac{ms}{s}\cos\phi\,ds, \quad . \quad . \quad (8)$$

where

$$\cos\phi=\frac{s\sin\theta}{\sqrt{s^2\sin^2\theta+k^2}},$$
$$d_3=\sqrt{s^2+k^2},$$

and

$$d_4=\sqrt{l^2+s^2+k^2-2ls\cos\theta}.$$

The total resistance of the system is then given by

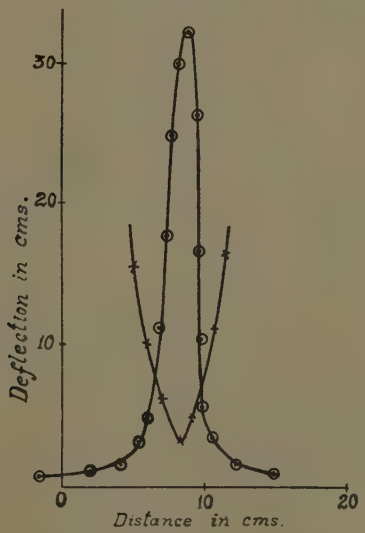
$$R_T=4(R_{44}-R_{43}+R_{41}-R_{42}).$$

Here, as in the previous case, R_{44} and R_{43} are calculated from equations (3) and (4). R_{41} and R_{42} are computed graphically from the integrals (7) and (8).

It has been shown analytically, and also observed experimentally, as described later, that there is hardly any loss due to radiation when the wires are bent as in fig. 4 and that there is considerable loss when they are bent as in fig. 2. The "physics" of these effects can be understood in the following manner. The directions of the electrical intensity in the plane containing the wires is obtained by joining a point on one of the wires to a similar point on the other wire lying nearest to it and having a phase difference of 180°. In fig. 4 the lines joining such similar points meet either of the wires at right angles. In fig. 2, however, such lines are not at right angles to the lengths of the wires. In fact they are parallel to the lines joining the ends of wires 1 and 2 or of wires 3 and 4. Now, in order that any dissipation of energy may occur it is essential that the electrical intensity must have some component along

the direction of the current in the wire. In fig. 4 the direction of electrical intensity being at right angles to the lengths of the wires—that is, to the direction of the current,—it has no component along the latter. Hence no dissipation of energy by radiation occurs. In fig. 2, on the other hand, the direction of electrical intensity being at an angle other than 90°, there is a component of it along the direction of the current. Hence dissipation of energy by radiation occurs.

Fig. 5.



The effect observed in the case of parallel wires, namely, that the radiation becomes appreciable when the separation of the wires is increased, can also be simply explained from similar considerations. When the separation is small all the electrical lines of force run from one wire to the other, cutting the latter at right angles. With increased separation the lines of force begin to run from one part to another of the same wire. In this case the directions of electrical intensity have components along the direction of current in the wire. Hence the dissipation of energy by radiation becomes possible.

Theory of the Resistance Measurement.

In a parallel wire transmission line the propagation constant is given by

$$\eta = \alpha + j\beta,$$

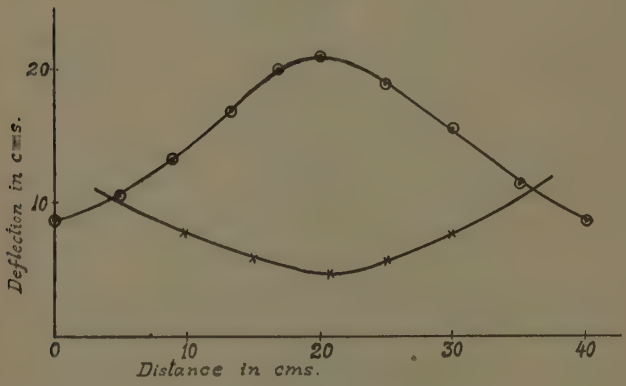
where

$$\alpha = \sqrt{\tfrac{1}{2}[(R+j\omega L)(G+j\omega C)+RG-\omega^2 CL]},$$

the attenuation constant,

and $$\beta = \omega\sqrt{CL},$$

Fig. 6.



the wave-length constant. If the leakance is small,

$$\alpha = \frac{R}{2}\sqrt{\frac{C}{L}}.$$

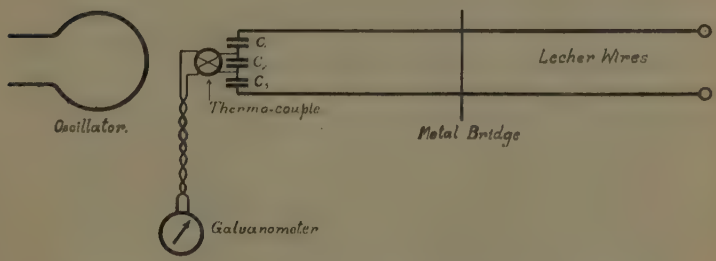
The experimental method consists in finding the value of α. C and L being known, R can then be calculated.

In order to find out α arrangements somewhat similar to those used for wave-length measurements are made. The resonance points are noted with the help of a movable bridge, and resonance curve is drawn between the deflexion of the indicating instrument and the position of the bridge along the length of the line on either side of the bridge. In order to obtain symmetrical resonance curves certain modifications after Laville [5] are made in the usual

arrangements, as shown in fig. 7. The indicating instrument, instead of being placed in the movable bridge, is connected with the bridge at the input end of the wires. The bridge, as seen in the figure, instead of being a simple metallic conductor consists of three large value condensers. Across the middle condenser the indicating instrument is connected. This method greatly improves the symmetry of the resonance curves.

A simple method of finding out the value of α is by a measurement of the so-called "half-width" of the resonance curve—that is, the distance between the points on either sides of the point of resonance when the deflexion of the indicating instrument becomes half of that at the

Fig. 7.



resonance point. If e be the half-width, we have the relation

$$e = \frac{n\alpha\lambda^2}{2\pi},$$

from which α can easily be calculated.

In order to obtain more accurate results another method, the theory of which is given below, was adopted [5].

If the deflexions in the indicating instrument are proportional to the square of the current, as is usual in high-frequency measuring instruments employing thermo-couples, the relation between the deflexion of the instrument and its position along the length of the wire, taking into consideration the bridge system at the input end, is given by [5]

$$\delta = A\frac{\cosh 2\alpha l - \cos 2\beta l}{\Omega},$$

where

$$\Omega=\cosh 2\alpha l-\cos 2\beta l+\frac{\alpha^2+\beta^2}{R^2+L^2\omega^2}\left\{P^2+\left(M\omega-\frac{1}{N\omega}\right)^2\right\}$$

$$\times(\cosh 2\alpha l+\cos 2\beta l)+\frac{2}{R^2+L^2\omega^2}\left[R\left\{\alpha P-\beta\left(M\omega-\frac{1}{N\omega}\right)\right\}\right.$$

$$\left.+L\omega\left\{\beta P+\alpha\left(M\omega-\frac{1}{N\omega}\right)\right\}\right]\sinh 2\alpha l$$

$$-\frac{2}{R^2+L^2\omega^2}\left[R\left\{\beta P-\alpha\left(M\omega-\frac{1}{N\omega}\right)\right\}-L\omega\left\{\alpha P\right.\right.$$

$$\left.\left.-\beta\left(M\omega-\frac{1}{N\omega}\right)\right\}\right]\sin 2\beta l.$$

If the coordinate system is changed so that the origin is taken at the point of the nth point of resonance, the above expresssion for Ω can be written as

$$\Omega=\left(\frac{n^2\alpha^2\lambda^2}{2}+2\alpha\lambda F+2B\right)+2l\left\{n\alpha^2\lambda(B+1)+\alpha F\right.$$

$$\left.+\frac{2\pi D}{\lambda}\right\}+\frac{8\pi^2l^2}{\lambda^2}.$$

When α is small, making use of the relation

$$\cosh 2\alpha l=1+2\alpha^2l^2,$$

it can be shown that

$$\delta=\frac{A}{\left(\frac{n^2\alpha^2\lambda^2}{4}+n\alpha\lambda F+B\right)+\frac{4\pi^2}{\lambda^2}l^2}.$$

In order to evaluate the constants we proceed as follows. We draw a curve (fig. 5) between l and $1/\delta$. Taking $l=x$ and $1/\delta=y$, the equation of this curve is

$$y=\frac{1}{A}\left\{\left(\frac{n^2\alpha^2\lambda^2}{4}+n\alpha\lambda F+B\right)+\frac{4\pi^2x^2}{\lambda^2}\right\},$$

which is a parabola-equation of type $y=qx^2+p$,

where $$p=\frac{1}{A}\left(\frac{n^2\alpha^2\lambda^2}{4}+n\alpha\lambda F+B\right)$$

and $$q = \frac{1}{A}\frac{4\pi^2}{\lambda^2};$$

$$\therefore \quad B + n\alpha\lambda F + \frac{n^2\alpha^2\lambda^2}{4} = \frac{4\pi^2}{\lambda^2}\frac{p}{q}.$$

In this equation p and q can be calculated from any two points on the parabola. B and F can be evaluated from the summits of two other consecutive parabolas. Knowing p, q, B, and F, α is calculated.

Experimental Arrangements and Observations.

An ultra-short wave oscillator generating 3 to 4 metres wave-length was built which was kept loosely coupled to the system of parallel wires. This system was bridged at input end with three condensers, of values $\cdot 25\mu$F. at the sides and 1μF. in the middle, which are shown in fig. 7 and explained in the last section. Across the middle condenser was joined a thermocouple with a sensitive low-resistance galvanometer. The deflexions of the indicating galvanometer for various positions of the bridge on either side of the resonance point were noted. From these the resonance curves were drawn and the resistance calculated by the method indicated in the previous section.

As a check on the measurement the observed values of α, when the distance between the wires was small, were compared with values calculated from the formula given by Mie [6]:

$$\alpha = \frac{1}{v}\frac{\sqrt{\mu\rho v/\lambda}}{2\sigma \log \frac{2k}{\sigma}}.$$

The agreement was always found to be good.

That the system of wires does radiate energy when bent in a particular manner or when widely separated was actually verified by observations made with an ultra-short wave-receiver. A milliammeter was placed in the plate circuit of the detector valve of the receiver, and the signal strength was measured by noting the deflexion of the milliammeter. The milliammeter indicated a steady deflexion due to the signal picked up directly from the oscillator. This deflexion was found to decrease when the distance between the wires was increased or when they were bent as in fig. 2 (a decrease of deflexion

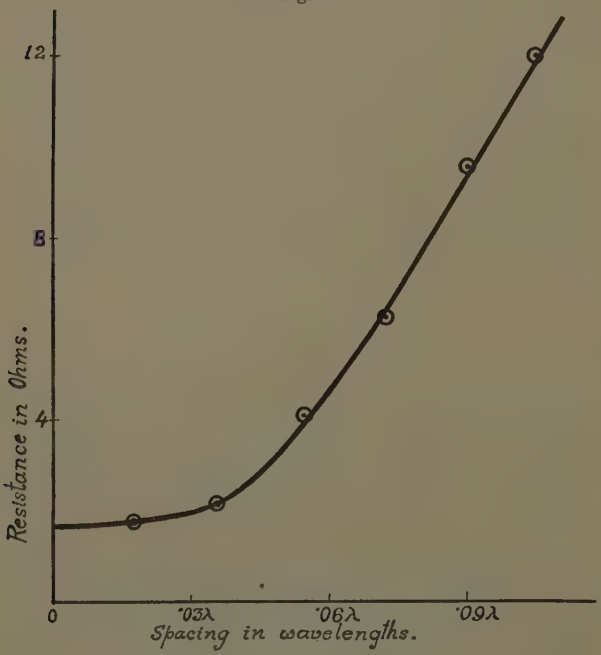
Case 1. *For Straight Parallel Wires.*

High-frequency ohmic resistance = 1·41 ohms.

TABLE I.

Spacing between two wires in wave-length.	Total resistance in ohms (observed).	Radiation resistance + ohmic resistance in ohms (calculated).
λ/60	1·66	1·56
λ/30	2·23	2·31
λ/20	4·06	4·43
λ/15	6·19	6·70
λ/12	10·04	9·59
λ/10	11·95	12·15

Fig. 8.



Change of the resistance as the spacing is increased.

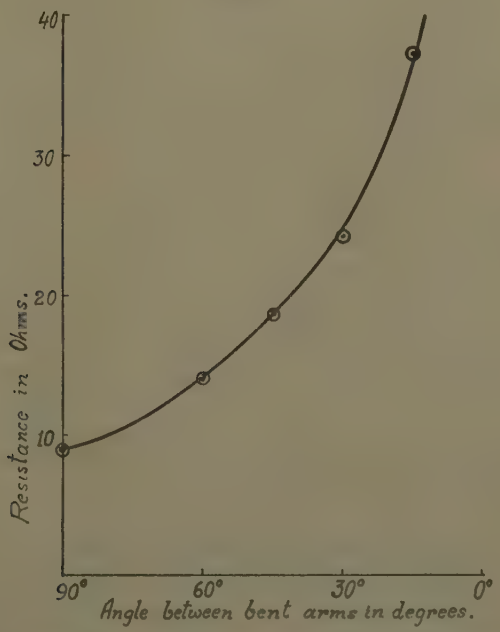
Case 2. *Wires Bent in their own Plane.*

High-frequency ohmic resistance = 2·16 ohms.

TABLE II.

Angle between the bent arms in degrees.	Total resistance in ohms (observed).	Radiation resistance + ohmic resistance in ohms (calculated).
90°	9·20	9·06
60°	14·04	14·39
45°	18·80	18·63
30°	24·20	24·22
15°	37·20	37·54

Fig. 9.



Change of the resistance as the angle between the wires is decreased.

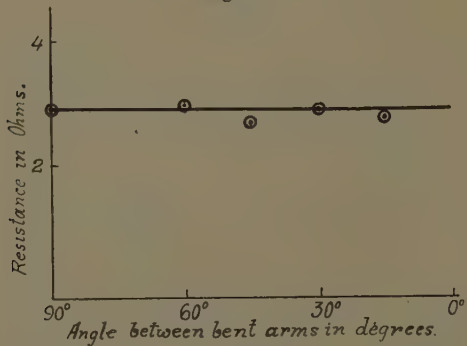
Case 3. *Wires bent such that the perpendicular to the plane containing the bent arms is parallel to the shortest length between the Wires.*

High-frequency ohmic resistance = 2·16 ohms.

TABLE III.

Angle between the bent arms in degrees.	Total resistance in ohms (observed).	Radiation resistance + ohmic resistance in ohms (calculated).
90°	2·84	2·71
60°	2·88	,,
45°	2·40	,,
30°	2·80	,,
15°	2·40	,,

Fig. 10.



Resistance for various angles between the bent arms.

indicating an increase of signal strength). When, however, the wires were bent as in fig. 4 the milliammeter-deflexion did not change at all.

The results of observations for the three cases discussed above are given in the Tables I., II., and III. In the third column the ohmic resistance, which is constant, is added to the calculated radiation resistance. This is because the measured values of the resistance gave the total resistance—that is, the ohmic resistance plus the radiation resistance.

Summary and Conclusions.

In the investigation described here the effect of bends on the radiation resistance of transmission lines has been studied both theoretically and experimentally. Two types of bends have been discussed : first, when the pair of wires is bent in the plane containing the wires, and second, when it is bent such that the perpendicular to the plane containing the bent arms is parallel to the shortest length between the wires. For the first case the radiation resistance has been found to increase with the decrease of the angle between the bent arms. The increase is rapid for angles less than 90°. For the second case the corresponding increase in resistance is very much less. It is therefore concluded that for practical purposes to minimize radiation losses unavoidable bends in a long transmission line should always be such that the perpendicular to the plane containing a pair of bent arms is parallel to the shortest length between the wires.

As a preliminary to the above investigation the variation in the radiation resistance of straight parallel wire system for various separations between the two wires has also been studied. The radiation is inappreciable for separations below $\lambda/20$; for separations beyond this the value of the radiation resistance increases rapidly.

The investigation was undertaken at the suggestion of Prof. S. K. Mitra, D.Sc., of the University College of Science, Calcutta, to whom I wish to tender my sincere thanks for interest and help in the course of the investigation. I further wish to express my deep gratitude to Prof. P. Dutt, M.A. (Cantab.), Head of the Physics Department, Hindu University, Benares, for the facilities and encouragement given to me.

References.

(1) Brillouin, *Radio Electricité*, April 1922.
(2) A. A. Pistolkors, Proc. I. R. E. xvii. p. 562 (March 1929).
(3) P. S. Carter, Proc. I. R. E. xx. p. 1004 (June 1932).
(4) R. Whitmer, Proc. I. R. E. xxi. p. 1343 (Sept. 1933).
(5) G. Laville, *Annales de physique*, tome ii. p. 328 (1924).
(6) G. Mie, *Annalen der Physik*, Band 2, p. 201 (1900).

Physics Laboratory,
Hindu University,
Benares, India.

LXIII. *Negative Ions of Iodine.*—Part I. *Probe Measurements*.* *By* JOHN L. SPENCER-SMITH, *Ph.D., Department of Physics, Queen's University, Belfast* †.

KNOWLEDGE of the effects of negative ions on the electric discharge through gases is extremely small. One ignores their possible presence, for example, in equations purporting to describe the discharge, such as those of Langmuir and Tonks ‡. With a view to obtaining further information about them, a new study has been made of one of the few low-pressure discharges in which it has been established that negative ions are present in large numbers, namely, ionized iodine vapour §, and is described in outline in this and a following paper ‖. For discharge theory it is particularly important to be able to measure negative ion concentrations; this can be done, and reasonably consistent data obtained, by modification of Langmuir's probe methods. The precision of the results will not be discussed here, since the present work is essentially a survey of a practically new field; the results are probably, however, decidedly better than order of magnitude data. The approximations involved are those introduced by consideration of an additional type of particle (the negative ion) not contemplated in earlier applications of probe analysis ¶ and those recognized as inherent in applications of Langmuir's original theory to complex systems such as the glow-discharge **. A natural development has been the production of rather strong beams of negative ions by a perforated probe ††; their strength agrees roughly with what would be expected from the modified probe analysis, and when they can be obtained of homogeneous composition they should provide a comparatively easily manipulated source for the study of the properties of negative ions.

* This paper includes part of a thesis submitted to the University of London for the degree of Doctor of Philosophy.

† Communicated by Prof. K. G. Emeléus, M.A., Ph.D.

‡ Langmuir and Tonks, Phys. Rev. xxxiv. p. 896 (1929).

§ *Cf.* Hogness and Harkness, Phys. Rev. xxxii. p. 784 (1928).

‖ A fuller account is contained in the author's Ph.D. thesis (London, 1934).

¶ Specific reference is considered unnecessary to the now well-known methods developed by Langmuir and his collaborators.

** *Cf.* Buchmann, *Zeits. f. tech. Physik*, xv. p. 179 (1934).

†† Part II.

One can usually in discharge problems obtain help from spectroscopic data. Spectra of the discharge have been taken as routine measurements in this work, but have proved to be of little value. In addition to the measurements described in this paper data have also been obtained for low-voltage arc-discharges in iodine and in mixtures of iodine and helium; the results are not reported, as they add nothing important to those obtained with the glow-discharge, with which they are in agreement.

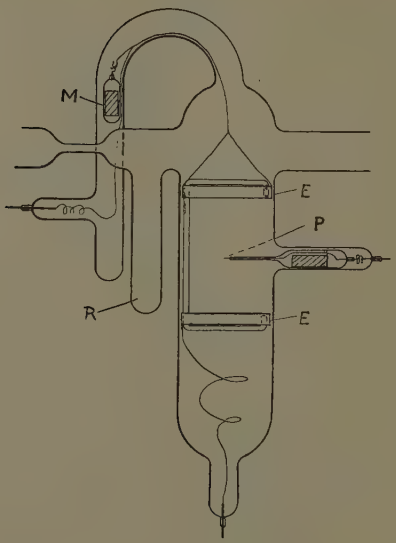
1. *Experimental Methods.*

Iodine was prepared from a commercial (B.P.) product. This was ground up with potassium iodide, sealed into a side distillation-tube on the main discharge-tube (*infra*) and fractionated over phosphorus pentoxide under vacuum into a small reservoir attached to the main tube (R), where it was condensed by liquid air cooling, and the distillation system previous to this sealed off. No evidence of impurity was found either spectroscopically or from the mass spectrum.

In studying the glow-discharge two types of tube have been principally used. Type I. is shown in fig. 1. The main electrodes (E) of nickel sheet, were held 4 cm. apart by thin quartz tubing, forming a cage system which could be moved vertically by a remote magnetic control (M). A cylindrical probe of 0·011 cm. diameter Mo wire (P), sheathed in glass to 0·5 cm. from the exposed end *, was situated in a side-tube, and could be moved across the discharge by a second magnetic control. By moving the cage system the probe could be put in any part of the discharge desired. Type II. (fig. 2) consisted of a cylindrical tube 6 cm. in diameter with plane parallel electrodes (Ni, 4 cm. $\times$ 12 cm.), separated to a distance of 3 cm. by pyrex rods, with their larger dimension along the tube. The Mo probe, similar to that used in type I., was suspended loosely in a side-tube, so that it could be moved between the main electrodes by tilting the main tube about a ground-joint in the pumping-lead. The size and material of the probe was varied in some tubes. It was found that corrosion of the metal parts by the iodine was greatly reduced by thorough degassing of the tubes,

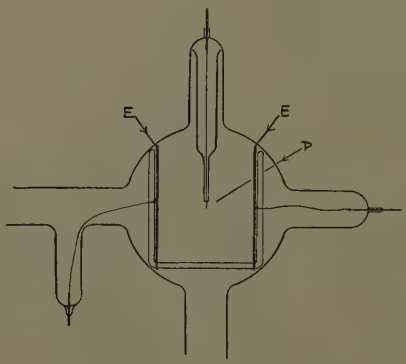
* *Cf.* Emeléus and Sloane, Phys. Rev. xliv. p. 333 (1933).

Fig. 1.



Glow-discharge-tube, type I.

Fig. 2.



Glow discharge-tube, type II., section.

in particular by specially careful removal of gas from the main electrodes in the preliminary treatment in the vacuum furnace before mounting, and by subsequent intensive inductive heating *in situ*.

The discharge-tubes were connected through two large liquid-air traps, separated by a tap with 2 cm. clearance in the barrel, to a 3-stage mercury-diffusion pump. Lubrication was by Burch's low-pressure grease, which does not give off gases when in contact with iodine *. When making measurements the discharge-tube had to be effectively isolated, otherwise the iodine would have distilled rapidly into the first liquid-air trap ; this was accomplished either by sealing off the tube or by lowering a glass bulb by a magnetic control into a constriction in the pumping-lead, or by removing liquid air from the near trap and closing the tap ; it was found immaterial which method was adopted. The iodine vapour pressure in the discharge-tube was controlled either by having the iodine reservoir in a temperature bath for pressures corresponding to lower than the room-temperature, or for higher pressures by putting the whole tube in a thermostated box. Values for the vapour pressure were taken from the International Critical Tables.

After a discharge had been run for several hours a slight tarnishing of the main electrodes was noticeable, although there was no falling off of current either to the main electrodes or the probe. It was, however, thought desirable to measure the resistance of the film which had presumably formed on the probe. For this purpose a type I. tube was used, and it was arranged that when the probe wire was retracted into its side-tube a contact consisting of a spring of thin platinum foil could be moved up magnetically and pressed against it, the resistance of the contact being then measured by a P.O. box. This resistance was found after the probe had been held for a few minutes at various potentials with respect to the space potential of the discharge in its neighbourhood, found by using the probe in the usual way ; before taking the resistance measurement the potential of the probe was always approached from a high negative value. Comparable results were obtained with 0·011 cm. diam. Mo and 0·08 cm. diam. Ni. In

* Van Praagh and Rideal, Proc. Roy. Soc. A, cxxxiv. p. 385 (1932).

both cases the films had their resistance unaltered by repeated removal and remaking of the Pt contact, and were reproducible after exposure to the discharge at different potentials. Table I. contains some results for the Mo wire, exposed in the negative glow of a discharge at 0·2 mm. pressure ; the electron temperature and concentration were 4·4 volts and $1{\cdot}8.10^7$/c.c. respectively, the positive ion concentration (from an i^2/V plot) 8.10^8/c.c. The width of the Pt. strip was 0·25 cm. and the area of contact, calculated on the assumption that the width of the contact region was equal to the radius of the probe wire, 0·0014 cm.[2] It was probably less, and the film resistance per unit area given probably an upper limit. Similar results were found with the Ni.

The explanation of the increase in resistance at the space potential is probably that at large positive potentials to the space the surface of the probe is kept clean by

TABLE I.

Resistance of Film on Molybdenum.

Probe potential relative to space ; volts	−40	−15	−5	0	+5	+20*
Film resistance ; ohms./cm.^{2}.	·006	·031	·181	·307	·105	·20

electron bombardment, whilst at large negative potentials it is kept clean by positive ion bombardment, but that near the space-potential the electrons or ions received have insufficient energy to destroy an incipient film. A similar effect has been recorded in adsorption of gases †. The resistances of the films are too small to cause discrepancies in the current-voltage characteristics for the probe, since the random electron current rarely exceeds 10^{-4} amps./cm.^{2}.

Confirmation of this conclusion was obtained by setting up a type I. tube in which the probe consisted of a hair-pin filament of Mo of the same diameter as before. The form of the characteristics of the probe was almost identical whether it was cold or at a bright red heat,

* Results for this and higher potentials are vitiated by arcing to the probe.

† Maclaren and Alty, Canadian J. of Research, iv. p. 498 (1931).

apart from the small additional electron emission current from the hot probe at negative potentials and a bodily shift of the characteristics about 2 volts in the negative direction with the hot probe, which could be reasonably attributed to heating of the vapour in its neighbourhood.

Separate tests made by F. D. Greeves and J. E. McF. Johnston in this laboratory have established that there is no error introduced in analysis of the discharge in iodine through change in the potential between the main electrodes consequent on alteration in the probe potential, under the conditions of the present experiments *.

In type I. tubes at pressures of iodine less than about 0·1 mm. there is no observable cathode glow and the cathode dark space is apparently non-luminous. The cathode edge of the negative glow is a deep indigo, changing to a colour which has been described as peach-blossom on proceeding towards the anode †. The Faraday dark space appears entirely dark. The tip of the positive column is a canary colour, and the main part of the positive column, which is uniform, and the anode glow purple. As the pressure is increased pale yellow striations may appear. These are unusually close together and are confined to the neighbourhood of the axis of the tube, except at their negative end, where they widen out and come close to the negative glow, which fills the tube laterally. At a pressure of 0·25 mm. the appearance of the positive column is reminiscent of a compact fish-skeleton. At still higher pressures a red cathode glow becomes visible and the cathode dark space turns a deep purple. The Faraday dark space is exceptionally short. The positive column retains its yellow tip, but the remainder turns purple and may be uniform or striated, and in sufficiently long tubes constricts to the form of a ribbon along the axis of the tube, in a manner usually only encountered in other gases under special conditions at generally higher pressures ‡.

At all pressures the potential required to maintain the discharge increases rapidly with increase in length of the positive column, showing the existence of a considerable longitudinal field. This cannot be due to a simple loss of energy in electron collisions, which would

* These will be reported elsewhere.
† Graetz's 'Handbuch,' Bd. iii. p. 754.
‡ Seeliger, *Phys. Zeits.* xxxiii. p. 273 (1932).

decrease the mean electron energy and increase the mobility, but must be ascribed to a diminution in the number of free electrons through attachment.

Typical discharge dimensions are given in Tables II. and III. The distance from cathode to positive column in helium under similar conditions would be >10 cm. The shortness of the cathode dark space in iodine is readily explained by the high mass of the positive ions of iodine, but the shortness of the cathode dark space and the high potential gradient in the positive column both require that the mean mobility of the negative carriers shall be

Table II.

Discharge-tube type I., diameter 3 cm. Pressure 0·12 mm. 500 volts between anode and cathode. Tube current $1{\cdot}4.10^{-5}$ amp./cm.^{2}

Cathode to cathode edge of negative glow	0·9 cm.
Approximate width of negative glow.....	0·9 cm.
Cathode to tip of positive column	3·1 cm.

Table III

Discharge-tube type I., diameter 3 cm. Pressure 0·20 mm. 570 volts between anode and cathode. Tube current $3{\cdot}9.10^{-5}$ amp./cm.^{2}

Cathode to cathode edge of negative glow	0·5 cm.
Approximate thickness of negative glow	0·35 cm.
Cathode to tip of positive column	2·2 cm.

very low, which is consistent with the presence of important numbers of negative ions.

2. *Probe Measurements.*

Application of Langmuir's probe analysis without specific reference to negative ions brings to light large discrepancies between the electron and positive ion concentrations. This appears to involve the presence of large numbers of negative ions and to involve a tendency to overestimate to an uncertain extent electron concentrations found by the semi-logarithmic method. Nevertheless the data so obtained give information about the discharge supplementary to rather than

superseded by the direct analysis for negative ions discussed in the following section.

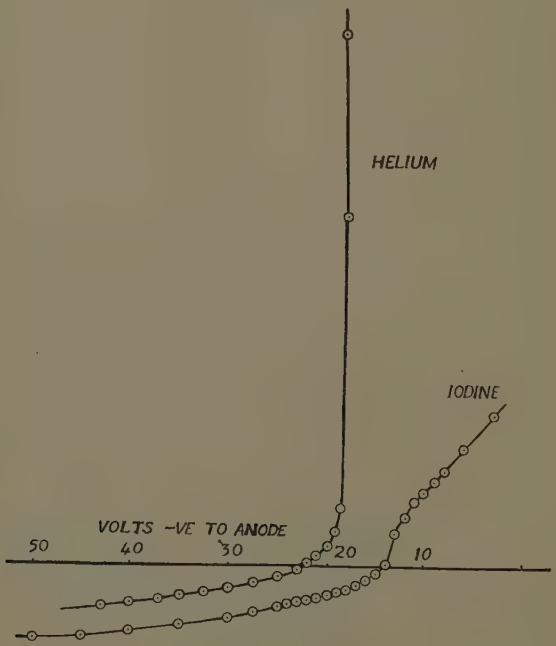
(i.) *Negative glow and Faraday dark space.*—There are two stable forms of Faraday dark space in iodine *. Neither shows marked reversal in potential. In the first there is a small approximately constant potential gradient and almost constant electron temperature and electron and positive ion concentrations. The second form is shorter, with an approximately constant potential throughout, but electron and positive ion concentrations falling off rapidly towards the anode. In both the electron temperatures are low. Typical probe measurements for the first are given in Table IV. There is a direct field of 5 volts/cm. There is also a great difference between electron and positive ion concentrations, the latter being about 10^2 times the greater, assuming the positive ions to be I_2^+†. This great discrepancy has been found from all probe characteristics taken in glow and arc discharges in iodine. Comparison between current-voltage curves for a probe in the discharge in iodine and in a gas which does not contain large numbers of negative ions, helium, is illuminating. Typical curves for negative glows in iodine and helium at comparable pressures, with currents in arbitrary units, are shown in fig. 3. In helium the electron current rises to a value several hundred times the positive ion current, whereas in iodine the electron and positive ion branches of the curve are nearly symmetrical. This incidentally introduces a new difficulty in interpreting the characteristics. The method of obtaining the electron current at negative potentials to the space is to assume that the positive ion current obeys the same law for small accelerating potentials for positive ions as for large ones, to extrapolate the line for large potentials to small, and to subtract the extrapolated current from the total current to obtain the electron current. In most discharges, where the electron and positive ion concentrations are nearly the same, the electron current under retarding potentials increases

* The existence of more than one stable form of discharge under apparently identical conditions of pressure and voltage has been noticed frequently in this laboratory, although rarely recorded in discharge literature; *cf.* Aston and Watson, Proc. Roy. Soc. A, lxxxvi. p. 167 (1911).

† This is not far from the truth; *cf.* Part II., *seq.*

rapidly as the space potential is approached, so that error in the positive ion extrapolation becomes rapidly negligible. In iodine the total electron current is not very much greater than the extrapolated positive ion current, and the error involved may thus become considerable, making the electron data more than usually approximate.

Fig. 3.



Probe characteristics.

In regions such as the negative glow and Faraday dark space, where the divergence of the electric field is small, the numbers of positive and negative charges per unit volume must be closely equal. Thus, in iodine the difference must be made up by presence of negative ions in numbers almost equal to the positive ions. This in turn introduces uncertainty into the interpretation of the semi-logarithmic plots for electrons received in a retarding

field, in that these at points close to the space potential include uncertain, but not necessarily negligible negative ion contributions. Whilst this will not affect appreciably the electron temperature, in judging which considerable weight is attached to more negative points of the semi-logarithmic plot, it will lead to an over-estimate of the random electron current, and hence of the electron con-

TABLE IV.

Tube type I. Tube voltage 500. Tube current density $1{\cdot}47.10^{-5}$ amp./cm.^{2}. Iodine pressure 0·12 mm. Electron concentrations from current at the space potential and electron temperature. Positive ion concentrations from linear i^2/V plot. Probably a few faster electrons were present.

Position of probe.	Space potential; volts −ve to anode.	Electron temperature; volts.	Electron concentration; 10^7/c.c.	Positive concentration; 10^9/c.c.
0·9 cm. from cathode. Close to negative edge of negative glow ..	42·5	1·4	9·5	9·7
1·13 cm. from cathode. Middle of negative glow ..	40·4	1·5	12·1	9·2
2·0 cm. from cathode. Middle of Faraday dark space	36·8	1·1	12·1	10·8

centration. In some cases a rather abrupt jump occurs on the semi-logarithmic plot 0·1–0·2 volts negative to the space. The corresponding current is of the order of the positive ion current, and so this jump may perhaps be due to the simultaneous failure of positive ions to reach the probe, and the reception of negative ions.

(ii.) *Positive column.*—Probe measurements have only been made in the uniform column, since it was found impossible to hold striations steady. Between the Faraday dark space and positive column there is a slight rise in potential and then a uniform potential gradient towards the anode. Typical data for the electron temperatures

etc. are included in Table V. In this case the positive column was not markedly constricted. The concentrations are lower than in the negative glow, but the electron temperature is higher, in accord with results for other gases *. The ratio of the electron and positive ion currents is of the same order as in the negative glow. The potential gradient in the positive column is high, and increases with increase in pressure for the current densities under consideration from some 30 volts/cm. at 0·12 mm. pressure to some 100 volts/cm. at 0·50 mm. pressure †.

TABLE V.

Tube type I. Tube voltage 500. Tube current density $4{\cdot}6.10^{-5}$ amp./cm.^{2} Pressure 0·50 mm. The positive column was uniform and not markedly constricted in this case.

Position of probe.	Electron temperature; volts.	Electron concentration; 10^8/c.c.	Positive ion concentration; 10^{10}/c.c.
Middle of negative glow	1·6	1·49	6·28
Positive column.....	13·5	0·35	2·05

3. *Further Consideration of Negative Ions.*

The idea that negative ions play an important part in iodine is not new, Mohler, for example, having observed them present in numbers comparable to the positive ions in a low-pressure beam-discharge ‡. When negative ions are present in considerable numbers information about them can be obtained by analysis of that part of the probe characteristic which corresponds to the acceleration of negative particles towards the probe, if allowance is made for the accompanying electrons, by a slight extension of Langmuir's theory of probes. At low pressures the negative

* *Cf.* Bramley, Phys. Rev. xxvi. p. 794 (1925).

† Similar negative glow and Faraday dark space data were obtained with type II. tubes.

‡ Mohler, Phys. Rev. xxvi. p. 614 (1926).

current flowing to a probe at potentials positive to the space is determined in the limit by one of two conditions :

(i.) Orbital motion around the probe occurs with cylindrical probes for low current densities and high electron temperatures in general.

(ii.) The negative current to the probe is limited by space charge when all the negative particles crossing the outer surface of the space charge sheath and moving inwards are drawn into the probe. The theory of this for electrons can be modified to include negative ions by observing that the effect of the presence of negative ions on the differential equation for this case * is equivalent to replacement of the electron random current i_e by

$$i_e+\Sigma i_n(m_n/m_e)^{\frac{1}{2}},$$

where the summation is taken over all types of negative ions present, i_n being the random current of ions of type n in the plasma, and m_n and m_e the mass of a negative ion and electron respectively. Assuming for simplicity that all the negative ions are of one type, the appropriate average of i_n is introduced, j say. Writing now

$$f=j/(i_e+j),$$

and calling I the total random negative current in the plasma, which can be found from the current to the probe at the space potential, inserting numerical values, Langmuir and Blodgett's solution takes the modified form

$$\mathrm{I}\left\{(1-f)+(m_n/m_e)^{\frac{1}{2}}f\right\}=1{\cdot}47\ 10^{-5}\mathrm{V}^{3/2}/(2\pi r^2.\ \frac{a}{r}\beta^2).$$

Currents are measured in amp., the potential across the sheath (V) in volts. r is the radius of the probe, a the radius of the outer surface of the space-charge sheath at voltage V, and β^2 is a known function of a, r *. The ratio a/r can be found at any potential V from the ratio of the total current to the probe at this potential to the current at the space potential, to which it is equal. End corrections and initial velocities are here neglected.

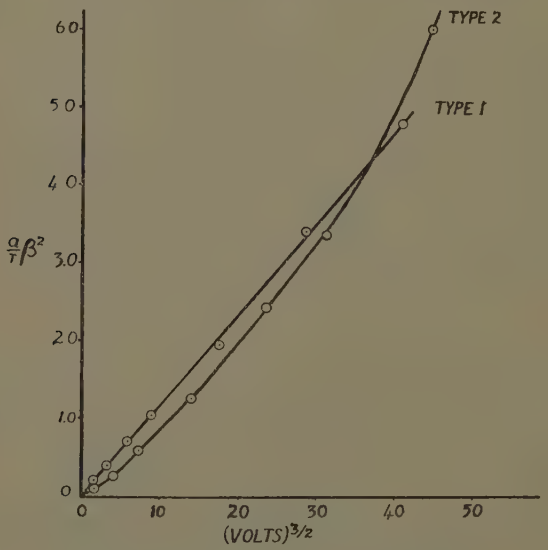
* Langmuir and Blodgett, Phys. Rev. xxii. p. 347 (1923).

In practice when $\beta^2 a/r$, found in this way, is plotted against $V^{3/2}$ the curves fall into two classes :—

(1) A straight line almost through the origin corresponding to space-charge limitation, as we require.

(2) A roughly parabolic curve, with $\beta^2 a/r$ increasing more rapidly than $V^{3/2}$. This type can perhaps be associated with orbital motion, and in fact gives almost a straight line when i^2 is plotted against V. Typical curves are shown in fig. 4 *. The equation was also tested for

Fig. 4.



Test for space-charge limitation of probe current.

electron reception in a low-voltage arc in helium, and found to agree well with observations except that the r.h.s. required to be multiplied by 0·8 ; this was introduced as a correcting factor in the iodine analyses †. For the

* It appears that the electron and negative ion currents are required to be space-charge limited. A more elaborate analysis could probably be developed for the case when the ion current alone was so limited, but it is questionable if data of sufficient precision could be obtained to warrant its application.

† Actually unnecessary in view of other uncertainties.

latter the calculations have been made as if the ions were I^-; in view of other uncertainties the improvement which would result if the appropriate mean were introduced (Part II.) does not appear worth the labour involved in the recalculation of results. Typical data are included in Table VI. The numbers for negative ions were found by first evaluating the r.h.s. of Langmuir and Blodgett's modified equation, using the experimental data reduced

TABLE VI.

Tube type I. Tube voltage 580. Tube current 3·0 10^{-5} amp./cm.^{2} Iodine pressure 0·18 mm. Positive ion random current found by extrapolating positive ion current to the space potential. Other data found as for previous tables.

Position of probe.	Space potential; volts —ve. to anode.	Electron temperature; volts.	Electron concentration; 10^7/c.c.	Positive ion concentration; 10^8/c.c.	Positive ion random current; amp./cm.^{2}.	Negative ion random current; amp./cm.^{2}.
Negative glow	40·4	1·5	12	92	$1·7\ 10^{-4}$	$1·7\ 10^{-4}$
Faraday dark space..	38·0	1·2	1·2	8·7	$1·4\ 10^{-5}$	$1·0\ 10^{-5}$
Just in the positive column	29·7	4·5	1·7	20	$2·8\ 10^{-5}$	$1·6\ 10^{-5}$

to a linear $\beta^2 a/r$ v. $V^{3/2}$ plot, whose slope was found, and then solving for fI. It is desirable to emphasize that the electron random current is greater than that of negative ions, and, in fact, greater than the tube current density; the electrons, even in iodine, are still responsible for transporting the major part of the tube drift current. Further, that the ease with which the data for iodine can be analyzed is closely connected with the large mass of the negative ions; it would be much more difficult to obtain data upon which reliance could be placed for negative ions in a light gas, such as oxygen.

It was not possible to obtain any one set of runs throughout a single discharge in which in all cases the current was limited by space charge. The numbers given are chosen from data for various discharges under nearly comparable conditions.

The negative ion random current is of the same order as the positive ion random current, confirming the conclusion drawn in the preceding section concerning the presence of negative ions in large numbers.

4. *Effect of Iodine upon the Discharge in Helium.*

Since negative ions appear to exert such a great control on the discharge in iodine it is interesting to see what effect iodine has upon the discharge in helium, which probably normally contains few if any negative ions. This investigation is of special interest in view of the use of electronegative gases in this way to form ribbon discharges.* It was hoped it would be possible to remove all iodine from the helium by cooling a side-tube in liquid air. However, even when this was done, and the discharge run under such conditions for several hours, the appearance was not that characteristic of pure helium, probably due to tenacious adherence of some iodine to metal surfaces in the tube, either free or as an iodide.

At a pressure of 0·9 mm. the glow discharge in He is very diffuse. The cathode glow is pink and there is a deep green cathode dark space. The negative glow is a whitish green, fading into the purple of the Faraday dark space. The distance between the cathode and the tip of the positive column is considerable, *e. g.*, 12 cm. The presence of even the unremovable trace of iodine previously mentioned has a marked effect. The cathode glow disappears, and the cathode dark space becomes colourless and reduced in length, the negative edge of the negative glow becoming simultaneously much sharper. The negative glow turns more yellow, with a pale blue edge on the cathode side, whilst the intensity of the luminosity falls off more sharply than before into the Faraday dark space, which is considerably reduced in length. When the partial pressure of the iodine is raised to 0·1 mm. the colouring of the discharge is almost like that of pure iodine, although the dimensions of the various parts

* *Cf.*, *e. g.*, Seeliger, *loc. cit.*

continue to alter somewhat as further iodine is added. Table VII. gives data for the thickness of the cathode dark space. A positive column had already appeared at a partial pressure of iodine of 0·1 mm., even with the main electrodes only 3 cm. apart, owing to the shortening of the Faraday dark space.

The shortening of the cathode dark space is probably due to heavy positive ions of iodine replacing the light positive ions of helium, the shortening of the Faraday dark space to the appearance of large numbers of negative ions of iodine. The latter conclusion is borne out by the results of probe analysis, all discharges in which there

TABLE VII.

Length of Cathode Dark Space in $He-I_2$ mixtures.

Helium pressure.	Iodine pressure.	Width of cathode dark space.
0·90 mm.	Nil.	2·3 cm.
0·90	Trace.	1·8
0·84	0·06 mm.	0·95
0·78	0·12	0·90
Nil.	0·13	0·95

For the pure He the tube voltage was 700, the current density 9.10^{-5} amp./cm.^{2}; for the remainder the tube voltage was 500, the current density 3.10^{-5} amp./cm.^{2}.

is any iodine present showing to some extent the peculiarities which have been observed in pure iodine. Typical data are given in Table VIII., obtained by the methods previously described. The first column for the ratio of electron and positive ion concentrations (n_e/n_p) was calculated on the assumption that the positive ions were all I_2^+, the second on the assumption that they were He^+; in either case there is a large discrepancy. For the pure He discharge the tube voltage was 700, the tube current density 9.10^{-5} amp./cm.^{2}, for the others the voltage was 500, the current density 2.10^{-5} amp./cm.^{2}.

In the first run, in pure He, there is accord between the electron and positive ion concentrations. The small trace of iodine in the second reduces the ratio n_e/n_p to

not greater than one-fifth, whilst the properties of the discharge with 0·14 mm. iodine are practically those of a discharge in pure iodine. It is satisfactory to notice that there is a simultaneous rise in the negative ion random current to a value practically identical with that for the positive ions. These data refer to the middle of the negative glow in a type I. tube, except for the pure He, for which data for the negative glow in another tube were supplied by F. D. Greeves. With 10^{-3} mm. iodine the space potential was 8 volts positive to the anode, there being no positive column, whilst it was 54 volts negative to the anode with 0·14 mm. iodine, due to the appearance of a positive column; since the latter was less than 1 cm. long there must again have been a large longitudinal field in it.

TABLE VIII.

Glow Discharge in Mixtures of Helium and Iodine *.

Helium pressure; mm.	Iodine pressure; mm.	n_e/n_p (I_2^+).	n_e/n_p (He^+).	Positive ion random current; amp./cm.^{2}	Negative ion random current; amp./cm.^{2}
0·90	Nil.	..	1·01	$1{\cdot}10\ 10^{-5}$	—†
0·90	10^{-3}	0·03	0·22	1·16 ..	—†
0·84	0·06	0·02	0·12	1·91 ..	$1{\cdot}40\ 10^{-5}$
0·78	0·14	0·01	0·07	2·05 ..	2·06

From general considerations it can be seen why negative iodine ions, even if formed at a rate decidedly less than positive ions, may exert a strong control on the discharge. This is because the negative ions will diffuse comparatively slowly towards the anode on account of their large mass, and, in contrast to the positive ions, will tend to concentrate near the potential maximum along the axis of the tube. The negative ions must thus largely disappear as a result of collision processes in the gas phase, which are in general inefficient compared with surface processes, and this will permit of the building-up of a large concentration of negative ions in the discharge.

* Current not space-charge limited.

† Similar results were obtained with low-voltage arcs.

Summary.

It is shown from general considerations that the glow-discharge in iodine at low pressures probably contains large numbers of negative ions. This is verified by Langmuir probe measurements, which show that the negative ion concentration is approximately equal to that of the positive ions and much greater than that of the free electrons, which may be of the order of 10^{-2} times smaller. A study of discharges in mixtures of helium and iodine demonstrates and to some extent elucidates the controlling effect exerted on the discharge by a strongly electronegative substance. Data are given in illustration of these statements.

This work was suggested by Professor Emeléus, and has been carried out under his supervision. I am indebted for financial assistance to Miss Pumphrey and Mr. Roger Clarke, and to the Council and Director of the Linen Research Association for leave of absence for several periods.

LXIV. *The Self-capacitance of Single-layer Coils.*

By W. Jackson, *M.Sc., Magdalen College, Oxford* *.

Summary.

The self-capacitance of a series of air-dielectric single-layer solenoids of 2, 3, and 4 inches diameter, and of length to diameter ratio extending from 0·25 to 4·1, has been determined from measurements of the natural frequency and by immersion in a liquid of known dielectric constant. It is shown that the self-capacitance is independent of frequency, and that the self-capacitance to radius ratio is independent of the radius for a given coil-shape. The results are compared with existing theories. A study has also been made of the effect of end-connexions, wire diameter, wire covering, and of the presence of a coil former on the effective self-capacitance. Finally, mention is made of a few measurements on 2- and 3-layer coils.

Acknowledgment is due to the Advisory Council of

* Communicated by Prof. R. V. Southwell, M.A., F.R.S.

the Department of Scientific and Industrial Research for a grant which made this investigation possible, and to Mr. S. Munday for constructing the coil formers. The work was carried out in the Engineering Laboratory, Oxford.

Introduction.

A LARGE amount of experimental evidence [1],[2],[3] has led to the conclusion that for all frequencies up to the natural frequency a single-layer coil, with its complex distribution of current and charge, behaves as though it had a uniform current throughout its length and a small fixed capacitance connected across its ends. In other words, that the low-frequency inductance can be regarded as operative up to the natural frequency, and that the distributed capacitance of the winding may be represented as a constant concentrated capacitance across the ends of the coil. Several attempts have been made to explain this fact mathematically, and at the same time to derive a general expression for the effective self-capacitance of single-layer solenoids as a function of the coil dimensions. The general conclusion has been to the effect that the important factor governing the magnitude of the self-capacitance C_0 is the coil-radius a, but that it is also a minor function of the shape of the coil as determined by the length to diameter ratio $b/2a$.

The experimental work available has not lent itself well to theoretical correlation, since, in general, it applies to coils wound and retained on formers of such materials as glass, ebonite, paxolin, etc. These augment the coil self-capacitance, but the magnitude of the increase has not been determined. As a result it is to be expected that the values obtained are larger than should be given by a satisfactory theory. The use in the present investigation of coils sensibly devoid of supporting dielectric has avoided this uncertainty, and it has also been possible to verify, by a new method, that the self-capacitance is indeed independent of frequency.

Description of the Measurements on Single-layer Coils.

Measurements of self-capacitance have been made on series of air-spaced coils of 2, 3, and 4 inches diameter

for a wide range of length to diameter ratios. This ratio extended from 0·25 to 1·35 for the 4-inch, 0·67 to 2·5 for the 3-inch and 2·0 to 4·1 for the 2-inch diameter coils. The coils were wound with No. 20 S.W.G. bare copper wire, with a pitch of 15 turns to the inch. The device employed in their construction was developed some years ago for an analogous purpose, and a description has been given elsewhere[4].

Two measurements were made on each coil, namely, of the true inductance L_0 and the natural frequency f_1. The inductance was determined, in the usual manner[5], by connecting the coil in parallel with a calibrated condenser, tuning the circuit so formed to resonance at a series of known frequencies provided by a high-frequency valve oscillator, and obtaining the slope of the straight line which resulted on plotting $1/f^2$ against C. (Howe found that this linearity continued up to the natural frequency; from this he concluded that the coil self-capacitance could be represented by a constant concentrated capacitance C_0 given in value by the intercept on the C-axis. Values of C_0 obtained by this method are not suitable, however, for correlation with theories which apply to simple solenoids, since the connecting leads from the coil ends cause a marked increase in the effective capacitance.)

The natural frequency of the coils was measured by the 'absorption" method[6]. For these measurements the end connexions were cut off level with the periphery, and the coil suspended in free space on long threads. The effective self-capacitance may now be derived as

$$C_0=\frac{1}{4\pi^2}\cdot\frac{1}{f_1^2 L_0}, \quad \ldots\ldots \quad (1)$$

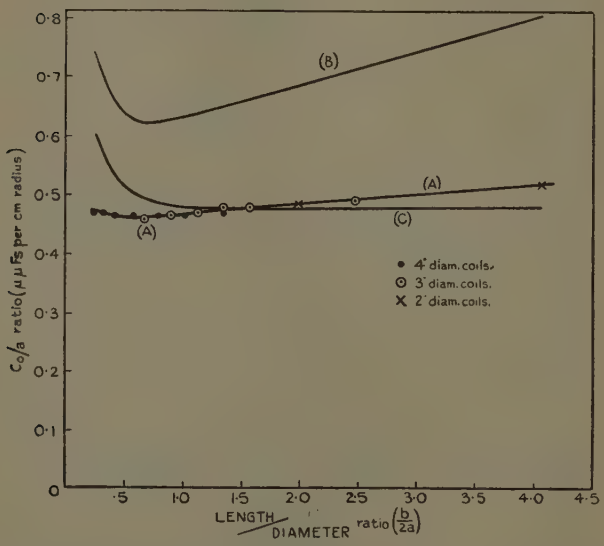
where L_0, as is shown later, may be taken as the true inductance.

The results of these measurements are shown in fig. 1, curve (A), where C_0/a, the self-capacitance in $\mu\mu$Fs. per cm. radius, is plotted against $b/2a$, the coil length to diameter ratio. It is seen that C_0/a is independent of a for a given value of $b/2a$, and that it appears to decrease slightly up to $\frac{b}{2a}\approx 0{\cdot}7$, after which it increases continuously from 0·46 to 0·51 as $b/2a$ increases from 0·7 to 4·0.

Determination of C_0 *by Coil Immersion.*

In order to verify that the low-frequency or true inductance is operative up to the natural frequency f_0—in effect to check the preceding method of determining C_0—use was made of the "Immersion" method suggested by Meissner[7]. This consists in observing the change in capacitance, as measured on a vernier condenser, necessary to retune the coil to a fixed frequency on its immersion

Fig. 1.



in a liquid of known dielectric constant κ. With an air-spaced coil of the type described, this immersion increases the effective self-capacitance κ times, so that if C is the capacitance change required

$$C_0 = \frac{C}{\kappa - 1}. \quad \ldots\ldots\ldots \quad (2)$$

Unfortunately, though not detrimentally, end-connecting wires could not be avoided in these measurements, since the coil is to form part of a resonant circuit. As a preliminary, therefore, the self-capacitance of the coil

with these end connexions—4 inches in length—was derived from a determination of its natural frequency. The coil was then suspended on its connecting leads from two terminals on an ebonite stripe spanning the open top of a cylindrical glass vessel 12 inches in diameter and 12 inches deep. For the coils on which results are to be stated this provided a depth of liquid of at least 4 inches in all directions around the coil after immersion. This should be adequate to embrace the electrostatic field of the coils concerned. The whole system was supported on insulators and was not earthed.

A liquid of reasonably high dielectric constant—butyl pthalate, $\kappa = 6{\cdot}78$ at 10^6 c.p.s.—was employed with a view to providing a large change on the vernier condenser. This liquid had the added advantage that it did not

TABLE I.

Description of coil tested.	Self-capacitance values ($\mu\mu$Fs).		
	With leads.		Without leads.
	By immersion.	By natural frequency.	By natural frequency.
4″ diam. 35 turns.	2·75	2·64	2·35
3″ diam. 40 turns.	2·30	2·23	1·77
2″ diam. 60 turns.	1·75	1·69	1·22

attack the paraffin wax ribs maintaining the coil-shape. The testing frequency was arranged to be 10^6 c.p.s. in each case, a frequency well displaced from the natural frequency of the coils. During the process of immersion liquid was poured into the vessel until its surface touched the coil-supporting terminals, and thus enveloped the full length of the coil end connexions.

The complete results for three coils of 4, 3, and 2 inches diameter respectively are given in Table I. It is seen that the values of C_0 obtained at 10^6 c.p.s. by immersion are in agreement to within 4 per cent. with those provided by the natural frequency determinations. From this it may be concluded that the self-capacitance, and hence L_0, are independent of frequency. The end connexions

are responsible for a variable increase in C_0 which reaches as much as 40 per cent. in the case of the 2-inch coil.

Theoretical Treatment of Coil Self-capacitance.

The theoretical problem may be stated briefly as follows. When a coil which is suspended in space without connexions is caused to resonate at its natural frequency, the magnetic field associated with the periodically changing current induces an E.M.F. throughout the coil. The current is zero at each end of the wire, and, corresponding to the actual current distribution along the wire length, there must be a charge distribution determined by the relation $\frac{\partial i}{\partial x} = \frac{\partial q}{\partial t}$. This latter produces a distribution of potential, and a resultant potential difference between the ends of the coil, which must exactly neutralize the E.M.F. distribution due to the changing magnetic flux. Not only must the total E.M.F. equal the resultant potential difference, but the current and charge over the coil must be such that the neutralization occurs at every point.

The extreme difficulty of determining the exact distributions from these facts compelled Howe [8] to approximate by assuming a sine distribution of current, and consequently a cosine one of charge, along the axial length of the coil, as shown in fig. 2*a*. He proceeded then to find the frequency at which the induced E.M.F. between the coil-ends due to the current is equal to the electrostatic potential difference due to the charges. These quantities may be calculated approximately by dividing the coil axially into a finite number of equal rings, in each of which the current and charge are taken to be uniformly distributed. The E.M.F. is given as $\Sigma i . \mathrm{M}w$, where i is the current round a ring and M the mutual inductance between this element and the whole coil. The potential difference is found from the known expression for the potential at a point—the end of the coil—due to a uniformly charged ring. On equating these, and regarding the self-capacitance as a concentrated quantity connected across the ends of the coil, C_0 is obtained in the form

$$C_0 = \frac{a}{1{\cdot}8 \times 10^{12}} \cdot \frac{\left(\frac{1}{L}\right) \Sigma(\mathrm{M} \sin \beta)}{[k\mathrm{F}(k) \cos \beta]_{\mathrm{av.}}},$$

where L is the total self-inductance, ΣM, of the coil and $F(k)$ is the complete elliptic integral of the first kind to modulus k. The quantities k and β are given by $\sin \alpha$ and $\pi \frac{z}{b}$, fig. 2 *b*, respectively.

The effective self-capacitance of a self-oscillating coil depends, therefore, only on the radius and on the shape of the coil. It remains to be considered whether C_0, as given by this expression, is really independent of

Fig. 2 *a*.

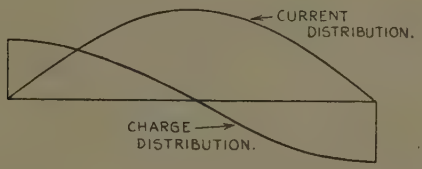
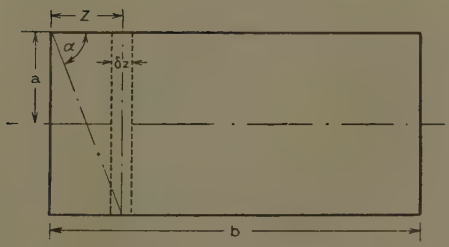


Fig. 2 *b*.



frequency. By connecting the coil to a condenser, resonant currents of lower frequency than the natural frequency can be caused to flow through it; the distribution of current corresponding to the charges on the coil will then be superimposed upon a uniform distribution of current corresponding to the charge on the external condenser. It is clear that the effective coil capacitance will continue to be given by the above expression if, but only if, the former distribution remains half a sine curve at all frequencies.

This expression for C_0 has been evaluated by Yamamoto[3] for a wide range of $b/2a$, and his values provide curve (B) of fig. 1. It is seen that the calculated and experimental

curves connecting C_0/a and $b/2a$ are quite similar: the former passes through a minimum in the region 0·5–1·0 of $b/2a$, as suggested by the measurements. The calculated values are higher throughout, however, to the extent of at least 30 per cent.

This observation, that equation (3) leads to too high a value of the C_0/a ratio for the air-dielectric coils to which it relates, is supported by Yamamoto's experimental work. His results, relating to coils with both ends insulated from earth, are in close general agreement with calculations from this formula. The coils tested were, however, all closely wound with D.C.C. wire on hollow glass cylinders and varnished. This combination of associated dielectric material, together with the presence of end-connexions, must have been responsible for making the effective self-capacitance appreciably greater than that of corresponding air-spaced solenoids. This applies equally to a diverse series of coils tested by Moullin [9].

In a recent treatment of the subject for coils of zero resistance and of a large number of turns, Zuhrt [10] represents the magnetic and electric fields as quasi-stationary potential fields. The self-oscillation current is supposed to consist of a Fourier series with unknown coefficients, and the natural frequencies are calculated from the roots of the infinite determinant obtained on satisfying the condition for coexistence of these fields and the boundary conditions at the open ends of the coil. The ratio of the wave-length λ_n of the nth harmonic frequency to the length of wire l is given in the form

$$\frac{\lambda_n}{l}=\frac{2}{n}\cdot\frac{b_e}{b}\sqrt{\frac{\mathrm{H}_1\mathrm{J}_1\left(jn\pi\cdot\frac{a}{b_e}\right)}{\mathrm{H}_0\mathrm{J}_0\left(jn\pi\cdot\frac{a}{b_e}\right)}}.$$

Here $$b_e=b\left\{1+\frac{1}{n}(0{\cdot}2+0{\cdot}3\sqrt{\frac{2a}{b}}\right\},$$

where b is the coil length and a its radius, and H and J are the appropriate Hankel and Bessel functions respectively. When this is evaluated for the fundamental and the result substituted, along with the calculated coil inductance value, in equation (1), it provides curve (C) of fig. 1 for C_0/a as a function of $b/2a$. This curve is in very close agreement with the experimental results except at low

values of $b/2a$, even though the coils under consideration have quite a small number of turns.

A theoretical discussion of the problem has also been presented by Breit[11]; this does not consider the coil in a self-oscillatory state, however, but as connected across the terminals of a condenser C. On equating the total self-induced E.M.F. due to the changing current to the P.D. between the condenser plates, expressed in terms of the charge and capacitance, an expression

$$\frac{1}{\omega^2} = \mathrm{L}\left\{\mathrm{C} + \int_{x_1}^{x_2} \frac{\mathrm{M}(x)}{\mathrm{L}} \int_{x_1}^{x} \frac{\alpha(x)}{\mathrm{L}} .dx.dx\right\}$$

is derived, in which $\mathrm{M}(x)dx$ is the mutual inductance of an element δx, at an arbitrary point x along the wire, to the rest of the coil, L is the self-inductance, and

$$\alpha(x) = \frac{\mathrm{Q}(x)}{(di_1/dt)}.$$

Here $\mathrm{Q}(x)dx$ is the charge between x and $x+\delta x$, and i_1 is the current at the condenser terminal. A comparison of the above with the experimental relation $\frac{1}{\omega^2} = \mathrm{L}(\mathrm{C}+\mathrm{C}_0)$ provides a general formula for the effective self-capacitance C_0. The computation of $\alpha(x)$ requires the nature of the coil surroundings to be specified, and Breit conceives a metallic shield in the form of a solid of revolution obtained by constructing an ellipse through the ends of the coil-length and revolving it about the coil-axis. By extending this shield to infinity subsequently, he shows that the effective capacitance of a short single-layer solenoid used with its centre-point grounded and undisturbed by surrounding objects is given by $\mathrm{C}_0 = 0{\cdot}0695p\ \mu\mu\mathrm{F.}$, where p is the perimeter of one turn; that is, $\mathrm{C}_0/a = 0{\cdot}436\ \mu\mu\mathrm{F.}$ per cm. radius. This compares well with the experimental values (fig. 1). Breit concludes that C_0 can be regarded as independent of frequency so long as the flux is the same through every turn; this applies in the case of short coils.

The effective self-capacitance of a coil suspended in free space, but grounded at one end, is given by the expression

$$\frac{\mathrm{C}_0}{a} = \left\{0{\cdot}436 + \frac{0{\cdot}378}{\log_{10}\left[16\left(\frac{2a}{b}\right)\right]}\right\} \mu\mu\mathrm{Fs./cm.}$$

Thus, for a coil of length equal to diameter $C_0/a=0{\cdot}75$. This may be compared with a value of 1·01 obtained for this shape by Hubbard [2] in his measurements on former-wound single-layer coils with one end earthed and with end-connexions attached.

A physical explanation of the passage of C_0/a through a minimum with variable coil length has been attempted by Casson and Cayrel [12] in a comparison of the two halves of a coil oscillating in a half-wave with the two equal and oppositely charged plates of a condenser. The capacitance of this condenser depends on (*a*) the intrinsic capacitance of the electrodes, and (*b*) the mutual capacitance resulting from the lowering of the potential of one by the opposite charge on the other. According as the electrodes are far apart or close together, so the condenser capacitance is determined predominantly by the first or second factor. Similarly, for the coil, the intrinsic (homopolar) capacitance of the positively charged half is larger the smaller the potential created by the charge on it, that is, the longer the coil. On the other hand, the negative charge on the other half-coil lowers the potential of the positive half more and more as the coil ends, where the charge density is greatest, are brought closer together. The resulting increase in the system capacitance from this cause is called the "heteropolar" capacitance. Thus

$$C_0=C_{hom.}+C_{het.}$$

and the effective self-capacitance exhibits a minimum, since $C_{hom.}$ varies from 0 to infinity, and $C_{het.}$ the reverse, as the coil-length is taken from 0 to infinity.

Effect of Wire Diameter.

The previous measurements have all related to coils wound with No. 20 S.W.G. bare copper wire, while the theoretical work mentioned takes no specific account of the wire diameter. It is of interest, therefore, to investigate whether the self-capacitance of a coil of given shape and of a constant number of turns per unit length is dependent on this factor. For this purpose a series of coils, each of 4 inches diameter and 40 turns, were wound with wire of diameter extending from 0·0096 to 0·0478 inch, and their self-capacitance determined from measurements of L_0 and f_1. The inductance value

is only a minor function of the wire diameter, so that it was determined directly for only one of the coils. The inductance of the others was then obtained indirectly from a comparison with this coil by a "double-beat" method in which the coils were employed in turn in the oscillatory circuit of a dynatron. The small inductance differences were calculated from the capacitance changes required in the circuit to maintain constant oscillation frequency.

The results of these measurements are given in Table II., and it is observed that C_0 increases sensibly linearly with d to the extent of about 10 per cent. over the range of wire diameter considered. It is clear that a theory of coil self-capacitance which does not take account of this factor cannot be regarded as complete.

TABLE II.

Wire diameter (inches), d.	·0096	·0142	·0180	·0219	·0280	·0365	·0478
L_0 (μ henrys) . .	141·7	141·1	140·8	140·5	139·9	139·4	139·0
C_0($\mu\mu$ farads) . .	2·180	2·205	2·225	2·250	2·295	2·350	2·445

A. J. Palmero[13] has recently presented a simple formula giving the self-capacitance in terms of the wire diameter d and the winding pitch s,

$$C_0 = \frac{2\pi a}{3{\cdot}6 \cosh^{-1}\frac{s}{d}} \mu\mu\text{Fs.}$$

where a, the coil radius, s, and d are in cm. The derivation of this was based on the mutual capacitance between two straight coplaner cylindrical conductors with their centres a distance s apart, and it is said to apply to single-layer coils when the length of winding is less than the coil diameter. For the first and last coils in the above table this formula gives C_0 values of 3·35 and 10·44 $\mu\mu$Fs. respectively. Although the variation with wire diameter is in the same direction as observed, the quantitative agreement cannot be regarded as satisfactory.

Effect of Wire Covering and of a Coil Former.

In order to determine the contribution of wire covering and of a coil former to the effective self-capacitance, four similar 4-inch diameter 40-turns coils were constructed, three, as previously described, on the special former, using bare, double-silk covered and double-cotton covered No. 20 S.W.G. wire respectively, and the fourth wound with bare wire on a similarly grooved paxolin former. The self-capacitance was again derived from the inductance and natural frequency values, the latter taken after the end connexions had been removed. The results of these measurements are given in Table III., from which it is seen that while the effect of the wire covering is small, that of the paxolin former is to increase the self-capacitance by more than 20 per cent. This result was confirmed in

Table III.

Air-spaced coils.			Paxolin former-wound coil.
Bare wire.	D.S.C. wire.	D.C.C. wire.	
$C_0 = 2{\cdot}32\ \mu\mu$Fs.	$C_0 = 2{\cdot}35\ \mu\mu$Fs.	$C_0 = 2{\cdot}38\ \mu\mu$Fs.	$C_0 = 2{\cdot}85\ \mu\mu$Fs.

measurements on a similar batch of 3-inch diameter 50-turn coils.

Measurements on Double- and Treble-layer Coils.

As an interesting extension to the previous work a series of measurements was made on double- and treble-layer coils built up from component 2-, 3-, and 4-inch diameter air-spaced single-layer solenoids. The 2- and 4-inch diameter coils were similar to those employed in the obtaining of curve (A), fig. 1, but the 3-inch coils used for this purpose were wound in reverse direction, so that when the coils were joined the inductive effects should be additive. The component coils were supported apart, at a uniform radial distance of $\frac{1}{2}$ inch, by a framework consisting of four pieces of thin paxolin strip extending the full length of the coils. This former was found to augment the self-capacitance of individual coils mounted on it by about 3 per cent. As before, the self-capacitance was

derived from equation (1) by measurement of L_0 and f_1, and the results relating to individual and combination coils of 20 and 30 turns per layer as given in Table IV.

As might be expected the self-capacitance of the three-layer coil is in each case intermediate between the values for the associated two-layer coils. Although the values for corresponding individual 20- and 30-turn coils are sensibly the same, the longer coils in combination possess distinctly higher values. This suggests some connexion between the self-capacitance as measured and the capacitance between layers when these latter are regarded as the plates of a cylindrical condenser. This connexion is not clarified very satisfactorily, however, by the results available ; for each of the 20-turn per layer

TABLE IV.

Turns per layer.	Individual coils C_0 ($\mu\mu$Fs).			Combination coils C_0 ($\mu\mu$Fs).		
	2″.	3″.	4″.	2″ and 3″.	3″ and 4″.	2″, 3″. and 4″.
20..	1·21	1·78	2·42	3·15	4·34	3·85
30..	1·22	1·78	2·40	4·15	6·04	5·17

two-layer coils the estimated capacitance between layers is closely 0·8 of the measured self-capacitance C_0, and for the 30-turn per layer combinations 0·9 of this value.

BIBLIOGRAPHY.

(1) G. W. O. Howe, Proc. Phys. Soc. Lond. xxiv. p. 251 (1912).
(2) J. C. Hubbard, Physical Review, ix. p. 529 (1917).
(3) I. Yamamoto, Inst. Elec. Eng. Japan, ccccxl. p. 259 (1925).
(4) W. Jackson, Wireless Engineer and E.W. v. p. 255 (1928).
(5) E. B. Moullin, Radio Freq. Meas. (2nd ed.) p. 338.
(6) E. B. Moullin, *loc. cit.* p. 345.
(7) A. Meissner, Jahrbuch der d. Teleg. ii. (1909).
(8) G. W. O. Howe, Journ. I.E.E. lx. p. 67 (1922).
(9) E. B. Moullin, *loc. cit.* p. 340.
(10) H. Zuhrt, *Archiv für Electrotechnik*, xxvii. pp. 613 & 729 (1933) : *Electrotechn. Zeits.* lv. p. 662 (1934).
(11) G. Breit, Physical Review, xviii. p. 133 (1921).
(12) P. L. Casson and J. Cayrel, *Comptes Rendus*, cxcviii. p. 1305 (1934).
(13) A. J. Palmero, Journ. Inst. Radio Engs. xxii. p. 897 (1934).

LXV. *A Note on Molecular Latent Heats.*

By J. D. Huffington *.

THE phase-change involving liquid and vapour is here regarded from the point of view of the general kinetic theory of gases and liquids as developed by R. D. Kleeman †. As a gas is compressed at constant temperature intermolecular attraction increases until finally the increase in attraction due to a small decrease in volume δv is great enough to balance the corresponding increase in expansion pressure δP_e. (The notation is that used by R. D. Kleeman.) The increased expansion pressure has two sources :—

(1) The molecules are crowded into a smaller volume.

(2) The mean kinetic energy of translation of each molecule is increased owing to the increased attractive forces.

When such a balance is reached the molecules will continue to do work in attracting one another until the expansion pressure becomes great enough to restore a balance again, the external pressure p remaining constant throughout the process, *i. e.*, at the start of a condensation and at the finish

$$\frac{\delta P_n}{\delta v} = \frac{\delta P_e}{\delta v}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where P_n=mean attractive pressure due to molecular attractive forces.

The general equation of state of the fluid is

$$P_e = p + P_n.$$

Thus from equation (1) a condensation is regarded as commencing or ceasing when $\delta p/\delta v$ or the elasticity is zero.

Considering 1 gm. mol. of molecules, let x be the work done in a condensation in producing the observed decrease in volume alone, neglecting from the start work which goes to increase the translational kinetic energy of the individual molecules. This division is a convenience which cannot be based on physical reality.

* Communicated by the Author.

† R. D. Kleeman, 'Kinetic Theory of Gases and Liquids.'

If v_1=vol. of saturated vapour,
v_2=vol. of saturated liquid,

$$x = R\theta \log \frac{v_1}{v_2},$$

i. e., x is the same as the work done in the isothermal compression of a perfect gas from v_1 to v_2, provided the following assumptions may be made :—

(1) Even distribution of molecules.
(2) Number of molecules unchanged during condensation.
(3) No energy expended on intra-molecular work.
(4) No change in molecular rotational energy.
(5) Size of molecules negligible.

The following table shows values of x/θ calculated for various substances, compared with L/θ or Trouton's ratio. Orthobaric densities and values for Trouton's ratio were obtained from the International Critical Tables.

Substance.	θ° K.	$R \log \frac{v_1}{v_2} = \frac{x}{\theta}$.	Trouton's Ratio $= \frac{L}{\theta}$.	$C = \frac{\text{Trouton's Ratio}}{R \log \frac{v_1}{v_2}}$.
HCl	188·1	12·3	20·7	1·68
CS_2	319·3	11·6	21·0	1·81
C_2H_5Cl	288·1	11·14	20·7	1·86
CH_4	114·1	10·63	19·4	1·83
C_2H_3N	353·1	13·06	20·2	1·54
C_6H_{13}	353·1	10·95	20·4	1·86
C_3H_5N	370·0	11·64	20·0	1·72
$C_4H_{11}N$	331·1	10·73	20·1	1·88
CH_3Cl	249·3	11·85	18·0	1·51
CH_4O	337·8	12·76	25·0	1·95
$C_2H_4O_2$	391·4	11·31	15·0	1·32
C_2H_6O	251·4	12·12	26·8	2·22
$C_3H_6O_3$	412·4	10·67	17·8	1·66
$C_4H_8O_2$	353·1	11·09	22·0	1·98
SO_3	326·1	11·87	29·2	2·45
C_3H_6	183·1	11·09	42·4	3·82
CO	81·1	10·34	17·5	1·70
O_2	90·1	11·0	18·1	1·65
N_2	77·3	10·2	17·3	1·70
H_2	20·4	7·7	10·8	1·40
He	4·29	3·9	5·1	1·31

Examination of the table leads to the conclusion that the correspondence between different substances at their boiling-points extends beyond the constancy of Trouton's

Ratio. x/θ is more constant than is Trouton's Ratio, extending over a range of substances and only becoming abnormal at low temperatures.

Considering for the moment substances for which Trouton's Rule holds :

$$\frac{L}{\theta} = \text{const.}$$

and

$$\frac{x}{\theta} = R \log \frac{v_1}{v_2} = \text{const.};$$

$$\therefore \quad \frac{L}{\theta} = CR \log \frac{v_1}{v_2},$$

where C is approximately constant.

Thus for these "normal" substances the following equations hold :

$$(1) \quad \frac{x}{\theta} = \text{const.},$$

$$(2) \quad \frac{y}{\theta} = \text{const.},$$

where

$$\frac{x}{\theta} + \frac{y}{\theta} = \frac{L}{\theta} = \text{const. (Trouton's Rule).}$$

Deductions.

The above facts have an important consequence, as follows :—

If P_n is the intrinsic pressure, Trouton's Rule may be stated approximately :

$$\int_{v_1}^{v_2} P_n \, dv = \text{const.}\ \theta;$$

$$\therefore \quad P_n = \text{const.}\ \frac{\delta\theta}{dv} \text{ between } v_1 \text{ and } v_2;$$

$$\therefore \text{ for saturated vapour, } P_{n_1} = \text{const.} \left(\frac{\delta\theta}{\delta v}\right)_1$$

$$\text{for saturated liquid } P_{n_2} = \text{const.} \left(\frac{\delta\theta}{\delta v}\right)_2.$$

But by the law of rectilinear diameters

$$\rho_1 + \rho_2 = a - b\theta,$$

i. e.,

$$\frac{M}{v_1} + \frac{M}{v_2} = a - b\theta.$$

M=molecular weight ;

$$\therefore \quad \left(\frac{\delta\theta}{\delta v}\right)_1 = \frac{M}{bv_1^2},$$

$$\left(\frac{\delta\theta}{\delta v}\right)_2 = \frac{M}{bv_2^2};$$

$$\therefore \quad \frac{P_{n_1}}{P_{n_2}} = \frac{\left(\frac{\delta\theta}{\delta v}\right)_1}{\left(\frac{\delta\theta}{\delta v}\right)_2} = \frac{v_2^2}{v_1^2}.$$

But it has been shown that

$$R \log \frac{v_1}{v_2} = \text{const.};$$

$$\therefore \quad \frac{v_1}{v_2} = \text{const.};$$

and

$$\therefore \quad \frac{P_{n_1}}{P_{n_2}} = \text{const.}$$

This equation seems to express a similarity of form taken by the fields surrounding different molecules, particularly at the point of phase-change. This similarity of form condition in the fields may be regarded in another way. Obviously a phase-change is a coordinated phenomenon involving interaction of all the molecules—when a phase-change takes place (whatever the temperature) it appears that the " structure " of the fluid is the same for different substances. The conception of " structure " recently introduced by Prof. E. N. da C. Andrade to the study of liquids might usefully be applied to all fluids if the above view is correct.

Temperature change will have the effect of destroying the particular structure indicated by P_{n_1}/P_{n_2} =const., and a phase-change will only take place when this structure is restored (*i. e.*, by changing the external pressure).

The above argument applies strictly only to " normal " fluids, but abnormalities due to degeneration at low temperatures or dissociation would not affect its general accuracy.

It appears that for normal and abnormal fluids C is a definite function of L/θ. In the following table C is

compared with a function of L/θ of the form $a+b\left(\frac{L}{\theta}\right)^n$. If L/θ is constant of course C is also constant.

Substances as above.	$1{\cdot}20+0{\cdot}00151\left(\frac{L}{\theta}\right)^2$.	C.
	1·85	1·68
	1·87	1·81
	1·85	1·86
	1·77	1·83
	1·82	1·54
	1·83	1·86
	1·80	1·72
	1·81	1·88
	1·61	1·51
	2·14	1·95
	1·54	1·32
	2·28	2·22
	1·68	1·66
	1·93	1·98
	2·39	2·45
	3·91	3·82
	1·66	1·70
	1·70	1·65
	1·65	1·70
	1·38	1·40
	1·24	1·31

The agreement is good on the whole. Exceptions are possibly due to errors in the experimental values used for L/θ or in the orthobaric densities involved in the calculation of C.

In conclusion, I wish to express my thanks to Mr. J. H. Awbery, of the National Physical Laboratory, for helpful suggestions and criticism.

LXVI. *On the Relation between Fusion and Strength.*

By Harold Jeffreys, *F.R.S., St. John's College, Cambridge* *.

IT was suggested by J. Johnston in 1911 † that elastic failure in a solid is the result of a real local melting, and the same author in collaboration with L. H. Adams developed the idea further in 1913 ‡. The fundamental

* Communicated by the Author.

† J. Wash. Acad. Sci. i. pp. 260–267 (1911).

‡ Amer. J. Sci. xxxv. pp. 205–253 (1913).

idea is that a solid begins to flow under a stress such that the melting-point is lowered to the actual temperature. The effect of stress on the melting-point is considered in three cases: (1) hydrostatic pressure on solid and liquid; (2) hydrostatic pressure on solid alone; (3) non-hydrostatic stress in solid, but with the normal stress the same in solid and liquid. Thermodynamical expressions for the effect of the stress on the melting-point are available in all cases. The first is unlikely to be applicable because it raises the melting-point in the majority of substances. The second gives Poynting's formula,

$$\frac{\partial \mathrm{T}}{\partial p} = -\frac{v\mathrm{T}}{\mathrm{L}}, \quad . \quad . \quad . \quad . \quad . \quad . \quad . \quad (1)$$

where T is the melting-point, p the pressure on the solid, v the specific volume in the solid state, and L the latent heat of fusion. In this equation the pressure on the liquid is supposed kept constant. The third has been considered by Riecke * and earlier by Willard Gibbs †. According to Gibbs,

$$-(\eta_{\mathrm{F}}-\eta)\,d\mathrm{T}+(v_{\mathrm{F}}-v)\,dp=\left(\mathrm{X}_{x'}+p\frac{\partial y}{\partial y'}\frac{\partial z}{\partial z'}\right)d\frac{\partial x}{\partial x'}+\mathrm{X}_{y'}\,d\frac{\partial x}{\partial y'}$$

$$+\left(\mathrm{Y}_{y'}+p\frac{\partial z}{\partial z'}\frac{\partial x}{\partial x'}\right)d\frac{\partial y}{\partial y'}, \quad (2)$$

where η denotes entropy, p normal pressure, xyz coordinates of a particle of the solid in the variable state, $x'y'z'$ its coordinates in an undisturbed state, and $\partial x/\partial x'$, etc., are strain components. Gibbs remarks that if the stress on the solid is hydrostatic, the coefficients of the changes of strain vanish; also for a solid in equilibrium with a fluid the normal is a direction of principal stress, and if we denote by P and Q the excesses of the other principal stresses over $-p$, and the corresponding strains by e_1, e_2, we have for unit mass

$$-(\eta_{\mathrm{F}}-\eta)\,d\mathrm{T}+(v_{\mathrm{F}}-v)\,dp=v(\mathrm{P}de_1+\mathrm{Q}de_2). \quad . \quad . \quad (3)$$

With P and Q zero this gives James Thomson's formula. But the parts of e_1 and e_2 produced by P and Q are given by

$$\mathrm{E}e_1=\mathrm{P}-\sigma\mathrm{Q}\,; \quad \mathrm{E}e_2=\mathrm{Q}-\sigma\mathrm{P}, \quad . \quad . \quad . \quad (4)$$

* *Ann. d. Phys.* liv. pp. 731–738 (1895).
† 'Collected Works,' i. p. 199.

where E denotes Young's modulus and σ Poisson's ratio. Then the right side is $\frac{1}{2}vd(P^2-2\sigma PQ+Q^2)/E$, and the depression of the melting-point, if we neglect the variation of L/T, is

$$-\frac{vT}{2LE}(P^2-2\sigma PQ+Q^2), \quad . \quad . \quad . \quad . \quad (5)$$

where L is in mechanical units. If, further, $Q=0$, this reduces to Riecke's formula.

Our first question concerns the range of physical validity of these expressions. If a solid and a liquid are in contact, but at different hydrostatic pressures, they are not in mechanical equilibrium, and we must consider how, without this condition, they can have the same free energy, as is necessary to the proof of equation (1). In many cases we can imagine that the solid liquefies, and that the liquid flows away to a place where the pressure is different, where it is brought to rest. But then the kinetic energy is either turned into heat by viscosity or into wave-motion by impact; in either case free energy is lost by the liquid, and the postulate for (1) breaks down. Lewis and Randall *, in proving (1) for a liquid and its vapour, suppose the two separated by a porous plug, the mechanical equilibrium being maintained by capillarity. Here the changes considered are reversible, though the influence of surface energy may complicate matters; but it is hard to see any analogue for a solid and a liquid. On the whole I am inclined to think that the conditions for the validity of (1) never occur in practice.

On the other hand, the conditions for (3) hold wherever a solid is in contact with its melt, and the integrated form will hold so long as the depression of the melting-point is not such as to produce substantial changes in L/T and E. Johnston and Adams comment on Riecke's remark that his relation is approximate, but this seems to be the only approximation involved, and similar ones occur if we try to integrate (1). It should be noticed, however, that (5) is subject to dp being zero, that is, that the pressure on the liquid is kept constant. If p and P vary by the same amount, the former will produce the greater effect in a ratio of the order of $E(v_r-v)/Pv$, which is in general large, since E/P can hardly be under

* 'Thermodynamics,' p. 183.

100 (1000 is more usual for rocks), while the expansion in melting is usually of order 1/10. There may be no change of p in a bar under a tensile test, but where a wire is drawn through a yielding mass the extra normal stress is probably comparable with those parallel to the interface.

Johnston and Adams integrate (1), neglecting the variation of L/v, which is probably legitimate to the accuracy aimed at, and find the pressure ϕ needed to bring the melting-point down to a standard temperature. The remarkable result is that, with barely significant exceptions, the order of increasing ϕ is also that of increasing strength. But when we actually compare the magnitudes we find that they are decidedly different. This is somewhat obscured in their paper, since the quantities are stated in different units; ϕ is in atmospheres (about 10^6 dynes/cm.^{2}), and the tensile strength in their column (c) in kilograms weight per mm.^{2} A few of the entries, translated into dynes/cm.^{2}, are as follows :—

	Tensile strength.	ϕ.	Ratio.
	$10^8\times$	$10^8\times$	
Pb	2·0	13·2	6·6
Sn	2·1	18·0	8·6
Zn	13	48·4	3·7
Ag	22	78·2	3·6
Cu	25	128	5·1
Pt	29	213	7·3

The actual strength is, therefore, in all cases substantially less than is given by the theory. The crushing strength in these metals does not appear to differ greatly from the tensile strength, as is easily seen by reference to standard tables. The theory, therefore, is open to three objections. The conditions for its validity seem to be unrealizable, the strength indicated is too high, and there seems to be no explanation of the fact that the metals yield almost equally readily to pressure and to tension. Nevertheless, the fact that the order of increasing ϕ is also practically that of increasing strength looks significant, even if we are not sure what it signifies.

The Gibbs-Riecke formula, being quadratic, meets the first and third objections. But for platinum Young's

modulus is about 4×10^{12} dynes/cm.^{2}, so that the depression of the melting-point by a stress equal to the strength is of order 1/1000 of that given by Poynting's formula. Quantitatively, therefore, this hypothesis fails to explain the facts. Further, while the ratios in the last column are not all the same, they do not show a variation by a factor of 10 in one direction, as would be expected if a quadratic formula was correct.

I have tried to apply the theory to some inorganic compounds, but in all but a few cases some of the data seem to be lacking. The results obtained are as follows :—

	t.	T_1.	L.	ρ.	ϕ.	Crushing strength.
					$10^8\times$	$10^8\times$
NaCl	800	1073	123	2·17	138	0·5
KCl	770	1043	108	1·99	112	—
Diopside	1391	1664	100	3·275	234	10 ?
Anorthite ...	1550	1823	105	2·765	276	10 ?
SiO_2	575	828	4·3	2·66	5·2	10 ?

Here ϕ is computed as before from the formula

$$10^{-6}\phi=95\cdot1\mathrm{L}\rho\log_{10}\mathrm{T}_1/\mathrm{T}_2, \quad . \quad . \quad . \quad . \quad (6)$$

where T_1 is the melting-point and T_2 is 25° C., both converted into the absolute scale ; L is in calories per gram. Silica is added for comparison, the data referring to the transition at 575°. For diopside and anorthite the theory is out by a factor of 20. According to the theory rock-salt shouid have about half the strength of diopside, and here again there is disagreement with experiment. If the data for silica had been taken for the true melting-point, ϕ would have been comparable with that for diopside ; but the transition at a lower temperature to a different crystalline form might appear more likely to be relevant. In any case the rough constancy of the ratio of ϕ to the strength that is found for metals does not appear to extend to compounds.

In all cases the strengths quoted refer to the materials as they occur ordinarily ; it is probable that the strength of a perfectly pure single crystal is zero, and that the actual strength is the result of such irregularities of structure as arise in the ordinary method of crystallization *. It

* *cf.* G. I. Taylor, Proc. Roy. Soc. A, cxlv. pp. 362–415 (1934).

seems to be sufficiently similar in different natural specimens of the same material to be considered a physical magnitude, though it can be greatly altered by subsequent treatment.

Although the formula of Johnston and Adams seems open to serious objections, it has certain good points that suggest that its utility is not exhausted. Thus, if $T_2 = T_1$, ϕ vanishes; that is, the strength should vanish at the melting-point, as it apparently does for most substances *. Also $d^2\phi/dT_2^2$ is positive, so that the graph of strength against temperature should be concave upwards; this agrees with Joffé's curves for rock-salt. The fact that the strength is a rather small fraction of ϕ may be attributed to the fact that the distortion of the crystal lattice in most types of yield is less drastic than fusion, so that L is not correctly put equal to the latent heat of fusion. Nevertheless it would not be surprising if the stress needed to distort the lattice permanently should be strongly correlated with L. The formula, treated as purely empirical, also represents the effect of general pressure on strength. For most substances the melting-point is raised by pressure, and if we ignore the arguments leading to (6), and simply consider the formula as it stands, it makes the strength rise with pressure, as it in fact does.

If, then, we suppose that for a given substance the strength is proportional to $\log (T_1/T_2)$, where T_1 is the melting-point at the actual pressure and T_2 the actual temperature, we can infer the variation of strength with temperature and pressure. Thus within the earth we have, on one theory of its thermal history, the following rough values :—

Depth (km.).	T_1.	T_2.	Strength (calc.).
			$10^9 \times$
0	1673	290	1·5
30	1800	900	0·61
300	2500	2250	0·092
1000	4700	4650	0·009

The values for zero depth correspond to an ultra-basic rock; the temperatures are taken from 'The Earth,'

* Joffé, 'The Physics of Crystals,' p. 40.

p. 154, with allowance for an extra cooling of 50° at great depths inferred later *. The support of mountains and the imperfections of isostasy suggest a strength of about 5×10^7 dynes/cm.^{2} at great depths. According to the formula this would be reached at a depth of about 500 km., which is probably too small ; but the comparison is, perhaps, worth recording in the hope that it may be improved.

LXVII. *Eddy Current Loss in Tube in Axial Alternating Magnetic Field.*

To the Editors of the Philosophical Magazine.

GENTLEMEN,—

IN a former paper † we solved this problem for the condition that the slope of the magnetic field at the inner radius $r=b$ was zero, *i. e.*, $\left(\frac{dH}{dr}\right)_{r=b}=0$. This restricts the analysis in sections 4, 5, 6 to thick tubes, where the inner radius is small compared with the outer. In the present communication this restriction is removed, and the results are valid in any case, provided the permeability is constant and e.m. radiation from the tube is negligible.

From (33) in f. p. the root mean square magnetic force at radius r is

$$H=A_1J_0(r)+B_1K_0(r), \quad . \quad . \quad . \quad . \quad (1)$$

where, for brevity, $J_0(r)$ signifies $J_0(mri^{3/2})$, $K_0(r)$ signifies $K_0(mri^{1/2})$, $m^2=4\pi\mu\omega/\rho$, μ=permeability, ρ=resistivity, and $\omega/2\pi$ = frequency. At the outer radius $r=a$, let $H=H_0$, then from (1),

$$H_0=A_1J_0(a)+B_1K_0(a). \quad . \quad . \quad . \quad . \quad (2)$$

From (37) in f. p. the r.m.s. current density at radius r is

$$\sigma=-\frac{1}{4\pi}\frac{dH}{dr}=\frac{mi^{3/2}}{4\pi}[A_1J_1(r)-iB_1K_1(r)], \quad . \quad (3)$$

from (1) by differentiation.

* M.N. R.A.S., Geoph. Suppl. iii. p. 8 (1932).

† Phil. Mag. xviii. p. 610 (1934), which will be denoted by f. p.

The rate of change of magnetic flux, $-\frac{dH_b}{dt}$, in the hole of radius b, induces at the inner circumference an e.m.f.

$$E=-i\omega H_b \pi b^2, \quad \text{for sine wave flux.} \quad (4)$$

The current in an elemental ring 1 cm. long of thickness dr is $dI=\sigma_b\, dr$, and the resistance of the ring is $2\pi b\rho/dr$. Thus the e.m.f. is

$$E=2\pi b\rho\sigma_b. \quad . \quad . \quad . \quad . \quad . \quad . \quad (5)$$

Equating (4) and (5), the current density at radius b is

$$\sigma_b=-i\omega b H_b/2\rho=\frac{-i\omega b}{2\rho}[A_1J_0(b)+B_1K_0(b)], \quad . \quad (6)$$

from (1) by substituting b for r.

When $r=b$ we obtain from (3),

$$\sigma_b=\frac{mi^{3/2}}{4\pi}[A_1J_1(b)-iB_1K_1(b)]. \quad . \quad . \quad . \quad (7)$$

Equating (6) and (7), since $m^2=4\pi\mu\omega/\rho$, we have

$$A_1\Big[J_0(b)+\frac{2\mu i^{1/2}}{mb}J_1(b)\Big]+B_1\Big[K_0(b)+\frac{2\mu i^{-1/2}}{mb}K_1(b)\Big]=0. \quad . \quad . \quad . \quad (8)$$

From (2) and (8) we find that

$$A_1=H_0F/[FJ_0(a)-GK_0(a)]$$
$$=H_0F/[FM_0(ma)e^{i\theta_0(ma)}-GN_0(ma)e^{i\phi_0(ma)}]; \quad (9)$$

$$B_1=-H_0G/[FJ_0(a)-GK_0(a)]$$
$$=-H_0G/[FM_0(ma)e^{i\theta_0(ma)}-GN_0(ma)e^{i\phi_0(ma)}]; \quad (10)$$

$$F=K_0(b)+\frac{2\mu i^{-1/2}}{mb}K_1(b)$$
$$=N_0(mb)e^{i\phi_0(mb)}+\frac{2\mu}{mb}N_1(mb)e^{i\{\phi_1(mb)+\frac{1}{2}\pi\}}; \quad (11)$$

$$G=J_0(b)+\frac{2\mu i^{1/2}}{mb}J_1(b)$$
$$=M_0(mb)e^{i\theta_0(mb)}+\frac{2\mu}{mb}M_1(mb)e^{i\{\theta_1(mb)+\frac{1}{2}\pi\}}. \quad (12)$$

In f. p. we derived the loss in the tube by integrating RdI^2 over the section. The result can be obtained much

more readily by applying Poynting's theorem. The power passing into the tube (per sq. cm. of outer surface), which is dissipated in heat, is $\frac{1}{4}\pi$ times the *real* part of the vector product of the electric (E_0) and magentic (H_0) fields at the outer surface.

Thus

$$P = -\frac{1}{4\pi} R\{E_0 H_0\} \times \text{outer surface area per cm. length,} \quad . \quad . \quad . \quad (13)$$

R denoting the real part.
Now from (3),

$$E_0 = \rho\sigma_0 = \frac{\rho m i^{3/2}}{4\pi}[A_1 J_1(a) - iB_1 K_1(a)]. \quad . \quad . \quad (14)$$

Whence from (13) and (14) the loss in ergs per sec. per cm. length of tube is

$$P = \frac{H_0 \rho m a}{8\pi} R\{A_1 M_1(ma) e^{i\{\theta_1(ma) - \frac{1}{4}\pi\}} + B_1 N_1(ma) e^{i\{\phi_1(ma) - \frac{1}{4}\pi\}}\}. \quad . \quad . \quad . \quad (15)$$

When the frequency is low and the thickness small, (15) can be expanded using Taylor's theorem, and we get

$$P = \pi H_0^2 \omega^2 a^3 t / 2\rho, \quad . \quad . \quad . \quad . \quad . \quad (16)$$

provided

$$\mu t/a \ll 1 \quad \text{and} \quad m^2 a t / 2\mu \ll 1,$$

where $t = (a - b)$. These two conditions correspond, respectively, to (1) the total flux in the metal section $\to 0$, whilst the current density is uniform; (2) the resistance of the tube ($2\pi a\rho/t$) $\gg$ the reactance ($4\pi^2 a^2 \omega$), which means that H within the hole is substantially equal to H_0 outside the tube. Using these assumptions, (16) can be deduced from simple theory. If *ma* and *mb* are large enough for the asymptotic formulæ on p. 617 of f. p. to be used in (15), and $x = \sqrt{2m(a-b)} > 4$,

$$P = \frac{H_0^2 \rho m a}{8\sqrt{2}\pi}, \quad . \quad . \quad . \quad . \quad . \quad (17)$$

which is the loss in a solid rod. To satisfy these conditions the screening ratio must be very large, so there is little flux within the hole and the e.m.f. induced at the inner surface is negligible.

The case of a very thin non-magnetic tube at medium radio frequencies, say $a=1$ cm., $t=0{\cdot}01$ cm., $n=10^6\sim$, falls between the above extremes, and it is preferable to compute the loss from (15), or to obtain it from curves or tables based on (15). Sections 5 and 6 in f. p. are easily modified to obtain the effective resistance and inductance of the energizing solenoid due to the core, under the general inner boundary condition.

London.
31 January, 1935.

N. W. McLachlan,
A. A. Meyers.

LXVIII. *On the Theory of the Barkhausen-Kurz Oscillations.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

MR. ALFVEN in your February issue * gives reasons for supposing that the BK oscillations are not due to the space-charge effects to which I attribute them †, but to the valve acting as "a negative resistance proportional to the emission." His original paper to which he refers works this out in detail. His mathematics are a little difficult, but they appear to be the general solution of a particular and simpler case considered by Mr. Morrell and myself as far back as 1922 ‡. We then came to a similar conclusion from energy considerations, proving that under certain conditions the work done by the alternating field on the electrons could be negative, and proportional to their number, which is, of course, the same thing as saying that the space has "negative resistance." At that time we also thought that this explained the Barkhausen oscillations.

Experiments in subsequent years, however, showed that the normal electron currents required to produce the oscillations were so large that the theoretical assumption that their space-charge effect could be neglected was untenable.

An investigation of the space-charges appeared to show that these alone could be more effective for generating

* H. Alfven, Phil. Mag, xix. p. 419 (1935).
† E. W. B. Gill, Phil. Mag. xviii. p. 832 (1934).
‡ Gill & Morrell, Phil. Mag. p. 161 (July 1922).

short-wave oscillations than the negative resistance effect; and it is this view I have endeavoured to put forward in recent papers.

Mr. Morrell and I only obtained a negative resistance by calculation if we assumed the anode to receive an (intermittent) electron current through the valve. Mr. Alfven's theory does not seem to require this condition; but we have never been able to maintain B–K oscillations without an anode current, and that at once introduces an intermittency which must be allowed for.

I have stated broadly that oscillations can only occur when the grid anode space is saturated, but more accurately the condition is that the space-charge nearing the anode must be just sufficient to reverse periodically the static field there. With varying currents traversing the valve this may occur when the average current is considerably less than the saturation current for the space.

Yours faithfully,

Merton College, Oxford.
13th February, 1935.

E. W. B. Gill.

LXIX. *A Valve-maintained Stretched-wire Vibrator.*

To the Editors of the Philosophical Magazine.

Gentlemen,—

THE Philosophical Magazine for October 1934 contains a paper by W. S. Stuart, "A Valve-maintained Stretched-wire Vibrator." The method described in that paper differs only in minor details from the one I proposed as early as 1929. My paper, of which I am enclosing a copy, appeared in the Russian 'Journal for Applied Physics,' vi. no. 6. Owing to the small circulation of Russian technical literature abroad, my paper has probably remained unnoticed, though, for the foreign reader, a brief summary in German has been added. That part of the summary in common with Mr. Stuart's paper is given below in English :—

"A circuit is suggested for producing sustained vibrations in a stretched wire.

"The conditions are determined for the production of sustained vibrations. The theoretical conclusions arrived at have been submitted to an experimental test.

" A circuit is suggested in which the back-coupling due to the ohmic resistance of the wire is balanced, thus allowing us to obtain sustained vibrations in very weak magnetic fields.

" The following practical applications of the method are suggested : stabilization of valve-oscillators of audio-frequency and its use for testing materials by means of a special acoustical method."

You would oblige me very much by publishing the contents of my letter in one of the next issues of your Magazine.

Yours faithfully,

Electro-physical Institute,
Leningrad.

H. V. BRAUDE.

LXX. *Notices respecting New Books.*

Magnetism and Matter. By EDMUND C. STONER, Ph.D. [Pp. xv+575.] (Methuen & Co., Ltd., London, 1934. Price 21*s.* net.)

THIS book is intended to replace the author's ' Magnetism and Atomic Structure ' which was published in 1926, at a time when the older quantum theory had been applied—with limited success—to magnetic problems. Since that date progress has been so rapid that, as Dr. Stoner states in his preface, a new book rather than additions and revisions to the previous one is called for. A glance at the references shows the reader that the developments of the last eight years occupy a considerable proportion of the book, whilst the experimental data has been considered closely in its relation to the present conceptions of atomic theory.

The book as a whole presents a comprehensive account of the magnetic properties of matter, and the author has achieved a commendable balance between the experimental and theoretical sides of the subject, and has at the same time maintained a suitable choice of material. The mathematics involved are adequate, but by no means heavy, and the book makes an easily readable exposition of magnetic theory.

Two minor points call for comment. An early chapter devoted to a brief account of the electrodynamic theory might well have been omitted. The last chapter of the book, dealing with metals and alloys, seems rather meagre, particularly as future developments in ferromagnetism seem likely to be found in the properties of ferromagnetic alloys.

Experimental Physics. By G. F. C. Searle, Sc.D., F.R.S. [Pp. xiv+363, with 129 figures.] (Cambridge University Press, 1934. Price 16*s.* net.)

This is the final volume of what may be termed Dr. Searle's Testament of Experimental Accuracy, and it contains accounts of a series of experiments in mechanics, elasticity, surface tension, viscosity, heat, and sound. These experiments are all described in the thorough manner with which most teachers of physics are undoubtedly familiar from his earlier volumes. There is no curtailment of discussion of important experimental or theoretical points; for example, a complete chapter on the mathematical treatment of many problems in surface tension forms a prelude to the description of the experimental technique. The typical sets of experimental data make very interesting reading, and the reviewer much appreciated the "honest" result of the determination of the mechanical equivalent of heat. The sections on sound are likely to be of great assistance to the many readers who will consult this book.

Numerical Studies in Differential Equations.—Vol. I. By H. Levy and E. A. Baggott. [Pp. viii+238.] (London: Watts & Co., 1934. Price 12*s.* 6*d.*)

This book will be welcomed by applied mathematicians, physicists, and engineers who need to make a numerical study of differential equations. The methods described have been developed and employed for over ten years in the instruction of students in the mathematical laboratory at the Imperial College of Science and Technology.

In the first two chapters graphical methods of solution are given. Methods for the numerical solution of a differential equation over a limited range are then discussed and the means of extending over a wide range of integration the tabulated values so found is described. This process of forward integration is applied to first order equations and extended to simultaneous equations and to equations of the second and higher orders. The importance of adequate checking of calculations is emphasized and systematic checks are incorporated as a part of the process of integration. The last chapter deals with special methods applicable to linear differential equations of the second order.

The book contains a large number of worked examples, and problems for solution are put before the reader.

[*The Editors do not hold themselves responsible for the views expressed by their correspondents.*]